DYEING WITH COAL-TAR
DYESTUFFS

DYEING WITH COAL-TAR DYESTUFFS

The Principles involved and the Methods Employed

BY

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AND

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FOURTH EDITION

BAILLIÈRE, TINDALL AND COX

7 & 8, HENRIETTA STREET, LONDON, W.C.2

1942

" The arts of bleaching and dyeing, which the habits and fashions of society have made important, are purely chemical."

From " Discourse Inductory to a Course of Lectures on Chemistry." SIR HUMPHRY DAVY (1802).

PREFACE TO THE FOURTH EDITION

THE request of the publishers for a fourth edition so soon after the third has convinced us that our method of treatment of the subject has been found satisfactory, and the general scheme of the book has, therefore, been retained. As in most other industries, rapid advances are being made in the dyeing industry, and the ever-widening demands on the trade, due largely to the introduction of new fibres and new finishing processes, have placed greater responsibilities on the dyer.

Feeling that this book is primarily of most value to the student we have thought it advisable to introduce three new sections, in order to make it more complete as a text-book. The section dealing with " Textile Fibres ; their Structure and Identification " has been added to meet the introduction of new synthetic fibres, which is proceeding rapidly ; it has also been deemed necessary, since some knowledge of the structure of fibres is essential in order to understand thoroughly the modern theories of dyeing. A section on the Preparation of Textile Materials for Dyeing has also been included. This collates and expands the somewhat scattered notes on this subject in the last edition.

Owing to the increasing adoption of dyeing machines by the trade a section on Dyeing Machinery has been included. This deals with principles, and does not attempt to catalogue the various makes of dyeing machines ; it should serve to give the newcomer to the industry a brief outline of the types of machines, which he may have to use.

All the other sections have been thoroughly revised and the most recent references to new work included. Some sections necessarily remain more or less static, whereas others, such as synthetic fibres with an affinity for wool dyestuffs, have required to be completely rewritten.

We are indebted to many colleagues for advice and help whilst writing this book. In particular to Mr. F. L. Goodall, M.Sc., for again reading and making valuable suggestions on the

sections dealing with Acid and Chrome dyestuffs, and to Dr. H. A. Thomas and Mr. C. P. Tattersfield for their general help and advice. For the illustrations, we are indebted to Mr. J. Such for the line diagrams; to Mr. Ken Satchwell for the excellent microphotographs of textile fibres; to Dr. T. H. Morton for photographs facing p. 133; to Mr. W. Kershaw for the microphotographs of "Rayolanda" and crease-resisted "Fibro"; and to the various machine makers for the loan of blocks. To all these we make grateful acknowledgment.

C. M. W.
C. C. W.

CHEADLE HULME,
May, 1942.

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DYEING WITH COAL-TAR DYESTUFFS

SECTION I.—GENERAL SURVEY OF DYEING

BEFORE the introduction of the coal-tar dyestuffs dyers, by using a limited number of chemicals and natural vegetable products, were able to produce a creditably wide range of shades. Their exclusive knowledge, acquired by long practice, was a very important factor in the early development of our textile industries and assisted in establishing British textiles as the best then obtainable. This factor in the evolution of our textile industry has usually been overlooked by most writers on the subject ; it has certainly never been appreciated at its true worth.

Perkin's discovery in 1856 of the basic dyestuff Mauve (C.I. 846), first introduced as Tyrian Purple and later known as Aniline Purple, is the true starting-point of the modern coal-tar dyestuff industry, since it was the first coal-tar dyestuff to be produced and used on a commercial scale. This dyestuff raised many problems with regard to its application on silk, wool, cotton, and mixed fabrics, as well as in calico printing, which were solved in conjunction with practical dyers and printers by Perkin who, although he had no training in the application of dyestuffs, was successful in solving some of its application problems. (See Rowe, *J.S.D.C.*, 1938, p. 555.) Cotton was dyed with the old dyewoods on a metallic mordant and then fixed with tannin, whilst Mauve was applied to cotton mordanted with tannin which had been subsequently fixed with the metallic salt, thus reversing the rôle of these substances.

Mauve was followed in 1859 by Verguin's discovery of a commercial process for the manufacture of Magenta (C.I. 677)

and by the introduction of several other basic dyestuffs, which enabled the dyer to obtain new shades on mordanted cotton in a single operation. All these early coal-tar dyestuffs were far from fast, which caused a slow-dying prejudice against " anilines." This stigma of being fugitive was still attached to the coal-tar dyestuffs long after extremely fast members had been adopted in the dyeing trade.

The next advance was the introduction by Girard and de Laire of the spirit soluble Rosaniline Blues (C.I. 689). These dyestuffs were insoluble in water and had to be dissolved in methylated spirit before adding to the dyebath, thus giving a fine dispersion of the dyestuff in water. By sulphonating these blues, Nicholson in 1862 was able to make them soluble in water, a discovery which enabled wool and silk to be dyed in brilliant shades from an acid dyebath. This was a great advance in simplifying dyeing, and the dyestuff known commercially as Nicholson Blue or Soluble Blue (C.I. 704) had a great vogue, and is still of the greatest service in the silk, jute, paper, and ink-making industries. It is at first curious that after the success of the Soluble Blues it was not until 1877—fifteen years later—that Caro sulphonated Magenta which was patented by the Badische Co., but this was doubtless because the necessary fuming sulphuric acid was in 1862 but a chemical curiosity.

The discovery of the diazo reaction by Peter Griess at Burton in 1858 (*Annalen*, 1858, 106, 123) has had more influence on the development of modern dyestuffs than any other chemical reaction, because the possible combinations for the production of azo dyestuffs are without limit, and hundreds are definite commercial successes. The range of acid, direct cotton, and mordant dyestuffs made by this reaction include practically every shade required ; their introduction and gradual development revolutionized dyeing methods in several branches of the trade, such as knitting yarns, carpet yarns, dress goods, cotton goods, etc. Meantime the synthesis of Alizarine (C.I. 1,027) by Graebe and Liebermann in 1868–69 had the ultimate effect of giving the dyer a range of dyestuffs superior in light fastness to the old wood dyestuffs. Their application did not involve great variation from the established methods except gradually to replace all mordants for wool except chromium, whilst the

bisulphite compounds of some alizarine dyestuffs were novel and involved the taking of special precautions in dyeing.

The patent taken out in 1871 by Schutzenberger and De Lalande for the dyeing of Indigo from the hydrosulphite vat, the British rights of which were bought by Read Holliday & Sons, Ltd., had the effect of introducing chemical control to the dyeing of this dyestuff as compared with the old fermentation vats, which demanded great skill and experience to keep them in good condition.

The next class of dyestuffs to be placed on the market were the azoic dyestuffs patented by Messrs. Thomas and Robert Holliday in 1880 (E.P. 2,757). This class of dyestuffs involved quite a new principle in dyeing as the process consisted of making the actual azo dyestuffs on the fibre, and so demanded from dyers a knowledge of dyestuff chemistry which had previously not been expected. The dyer had to understand the reason why diazotizing must be carried out cold, why the diazotized material must be protected from light and heat, and why certain developing baths had to be alkaline whilst others had to be acid. This principle of producing insoluble dyestuffs on the fibre received a great extension in 1912 when the firm of Griesheim-Elektron introduced Naphtol AS (E.P. 23,732 of 1913), the forerunner of the present important series of dyestuffs of this class.

An important landmark in the history of dyeing was the discovery by Böttiger in 1884 of Congo Red (C.I. 370), which was the first member of the direct cotton dyestuffs to be marketed. These dyestuffs have led to a great simplification of the cotton dyer's work, to the development of single bath union dyeing and, as a natural corollary, to modern garment dyeing. How useful these dyestuffs have been is shown by the fact that of the British output in 1938—19 per cent. represented direct cotton dyestuffs.

The direct cotton dyestuffs were followed by the discovery of Primuline (C.I. 812) in 1887 by Green, whose main use again necessitated the taking of special precautions similar to those required by the azoic dyestuffs.

In 1873 the French chemists Croissant and Bretonnière produced the first sulphur dyestuff Cachou de Lavel (C.I. 933), but there was no further outcome of this discovery until 1893

when Raymond Vidal patented the sulphur dyestuff known as Vidal Black (C.I. 973), which was the real progenitor of this important class of dyestuffs. These dyestuffs greatly simplified the production of fast shades on cotton, but again placed greater demands on the chemistry of the dyer in that he had to dye with leuco compounds, which required to be in a perfectly reduced and soluble state, whilst it also involved careful handling of the material in order to get level results. A number of these dyestuffs have recently been put on the market in a solubilized form by the I.G. under the name Immedial leuco dyestuffs.

The introduction in 1900 by the Berlin Aniline Co. (E.P. 8,874 *J.S.D.C.*, 1901, p. 67) of the metachrome process for the application of certain mordant dyestuffs again made it desirable for the foreman dyer to understand the chemical reactions taking place in the dyebath in order to get successful results, although when these were thoroughly understood it led to a simplification of his work.

Perhaps the biggest demand of any class of dyestuffs on the skill and chemistry of the foreman dyer was made by the discovery of Indanthren Blue (C.I. 1,106) in 1901 by René Bohn. This dyestuff and succeeding members of the vat dyestuff series were found, in general, to possess a fastness far excelling other known dyestuffs, and so revolutionized the standards of fastness in cotton textiles. In order to simplify the dyeing process many attempts were made to stabilize the very unstable reduced forms of the vat dyestuffs. Success was eventually obtained independently in 1922 by Bäder and Sunder, and by Scottish Dyes (now absorbed in Imperial Chemical Industries, Ltd. (Dyestuffs Section), which resulted in the introduction of the Indigosol and Soledon dyestuffs respectively.

About 1924 the Neolan series of wool dyestuffs containing chromium in the molecule were introduced. These dyestuffs have dyeing characteristics very similar to those of the acid dyestuffs, but in their fastness properties on the fibre they are related to the chrome dyestuffs.

The development of synthetic fibres provided the dyer with further problems which resulted in the introduction of special series of dyestuffs for the dyeing of these fibres. In the case of viscose rayon dyestuffs giving uniform shades on viscose of

varying dyeing affinity had to be selected, and this led to the production of the level dyeing Icyl, Benzo Viscose and Rigan dyestuffs. Acetate rayon possessed no affinity for the then existing cotton and wool dyestuffs, and the first attempts to dye it were so unsuccessful that the possibility of its use on a commercial scale was seriously threatened. This led to much work on the production of dyestuffs suitable for the dyeing of acetate rayon, culminating in the introduction by Green and Saunders in 1922 of the Ionamines (*J.S.D.C.*, 1923, page 10 ; 1924, page 138), which are temporarily solubilized derivatives of insoluble aminoazo compounds, and a little later by the Duranol, S.R.A. and Dispersol dyestuffs. The latest advance in this field was the introduction in 1936 of the water soluble Solacet dyestuffs.

Within recent years the field of synthetic fibres has been extended by the introduction of casein fibre, basified fibres, such as " Rayolanda " X and " Vistralan," nylon and vinyon. These fibres present specific dyeing problems so that it is necessary for the dyer thoroughly to understand their individual dyeing peculiarities, both when dyed alone and in conjunction with other fibres.

There are two new series of dyestuffs which were being developed and expanded at the present time ; these are the Carbolan dyestuffs, which are acid dyestuffs whose fastness to washing has been improved by the introduction of a long paraffin chain in the molecule, and the dyestuffs derived from the Phthalocyanine pigments, the first of which was put on the market under the name of Durazol Fast Blue 8GS.

The above résumé clearly illustrates that though dyeing processes have been simplified they have also made an increasing demand upon the chemical knowledge of the dyer, and the new classes of dyestuffs instead of depreciating the dyer's status are increasing it. True the old secrecy of recipes has passed away but no recipe, however elaborately bound in gilt and leather, ever made a dyer. The more experience one has in a dyehouse the more does one realize that the success of the dyer depends equally upon the keenness of his observation and his common sense as upon his knowledge of the application of dyestuffs.

The golden rule of dyeing is that compound shades should be dyed with dyestuffs which dye on at the same rate, but many other practical considerations prevent this rule from being followed in every case. In this connection one must stress very forcibly the individuality of dyestuffs both as regards dyeing and fastness properties, etc. The more one subjects dyestuffs to a detailed examination of their dyeing properties the more apparent it becomes that it is impossible to forecast from the behaviour of any one dyestuff what will be the behaviour of other members of the same class. This question of the individuality of dyestuffs appears to be one aspect of dyeing which, except in a few cases, has been either completely overlooked or deliberately neglected. Numerous examples of this individuality may be found in the text of this book, but the following specific examples will serve to emphasize the wide differences shown by members of the same class of dyestuffs.

Statements that the direct cotton dyestuffs are dyed with 5–20 per cent. salt may be found in most instructional pattern cards dealing with the dyeing of these dyestuffs, yet included in this group are members showing very wide differences in salt sensitivity. This is illustrated by the following percentage exhaustion results obtained on 150/27 viscose by dyeing in a liquor to yarn ratio of 10 to 1 for $\frac{1}{2}$ hour at 90° C.

Dyestuff		Percentage Salt						
		0	0·1	0·3	0·5	1·0	5·0	10·0
		%	%	%	%	%	%	%
0·5% Benzo Purpurine 4B 180% ..	..	82	94	97	98	98	100	100
0·5% Durazol Violet 2 BS ..	..	7	10	15	20	30	65	79
0·5% Diphenyl Fast Blue Green BL	..	19	28	40	47	70	100	100
0·5% Paramine Black BH 240%	..	46	52	63	73	82	93	95
0·5% Chlorazol Fast Orange AG ..	..	19	26	36	47	63	91	95
0·5% Chlorantine Fast Blue GLN	..	20	30	52	64	83	100	100

It is easy to see from these figures that to get the best results with direct cotton dyestuffs the instruction that " direct cotton dyestuffs are dyed with 5–20 per cent. salt " is totally inadequate ; this is particularly so when dyeing compound shades.

Again, if one examines the rate of dyeing at 90° C. in a liquor

to yarn ratio of 10 to 1 without salt, such widely differing results as the following are obtained :

PERCENTAGE EXHAUSTION ON 150/27 VISCOSE

Dyestuff	2 mins.	4 mins.	6 mins.	8 mins.
	%	%	%	%
0·5% Chlorazol Fast Black BK 200% ..	2	5	10	12
0·5% Benzo Purpurine 4B 180% ..	10	24	38	47
0·5% Chlorazol Fast Yellow 5GKS ..	21	40	45	47
1% Chlorazol Black BKS	25	28	28	29
0·5% Chlorazol Fast Orange G	41	44	46	48
0·5% Chlorantine Fast Blue GLN 200%	Exhaustion too small to estimate.			

Dyestuff manufacturers have to-day greatly extended the scope of the information they supply about their products, particularly with regard to those properties to which a number may be attached, but the lack of specific information about the less easily measured and tabulated properties has one very unfortunate effect. The foreman dyer is a conservative creature immediately concerned with day to day production, and when a new dyestuff appears its adoption means that he has to learn all its tricks in the school of bitter experience, and does not always welcome its advent so readily as might be desired. This justifies reiterating the plea " that the dye makers should supply such information as sensitivity to salt, effect of temperature, etc., of dyes, in order to help further in consolidating the goodwill between them and the consumers " (see Wilcock, *J.S.D.C.*, 1939, p. 440).

The trends of modern dyeing may be separated into five phases :

1. The increasing adoption of mechanical and labour-saving appliances.
2. The constant demand for ease of application.
3. The increasing scientific knowledge required to understand thoroughly the application of the modern coal-tar dye-stuffs and auxiliary products.
4. The increasing number and variety of fabrics made from combinations of natural and synthetic fibres.
5. The increasing call on the dyestuff manufacturer and dyer for dyeings capable of withstanding new treatments

during manufacture, thus allowing cloths of new or improved quality to be manufactured.

By its increasing adoption of machines, the dyeing industry is only following the economic conditions ruling in all industries at the present time, viz : that increased cost can only be met by increased production. This explains why machines capable of dyeing 1,200–1,400 lb. of wool are being adopted, whereas 250 lb. only was formerly dyed at a time ; whilst machines capable of dyeing 2,000 lb. of loose cotton are also to be found. The desire to economize labour is also responsible for the increasing number of machines for the dyeing of yarns in the form of cops, cheeses, and beams which are being steadily adopted in order to avoid winding the yarn into hanks and then re-winding into cops, etc. For the same reason pack dyeing machines for dyeing hanks and warps are now being widely used, particularly in cotton dyehouses. As a uniformly wound package—termed a " cake "—is formed in the Topham spinning box as part of the process of the manufacture of viscose rayon, it is not surprising that, for economic reasons, attempts should be made to dye viscose rayon in the " cake " form. Yarn dyed in this form can, for example, be coned or warped directly from the cake, which is a cheaper method than winding into skein form for dyeing and then coning or warping. Very good results have recently been obtained, but this method of dyeing can only be regarded as being in its early development stage.

From the first phase it is a logical step to the second phase. Modern economic conditions enforce economy in labour, time, and steam, so that it is natural for the dyeing industry to prefer those dyestuffs which are most readily applied, particularly as—in general—the less a material is handled the less is its condition depreciated. This reason accounts, in many cases, for the increasing preference given to the higher priced Indigosols and Soledons over the vat dyestuffs and for the use of the Fast Colour salts, which only require to be dissolved in water instead of the Fast Colour bases which require diazotizing before use. Again, successful pack dyeing requires soluble dyestuffs, as any insoluble matter will be filtered out by the material, thereby soiling it ; for this reason true alizarine dyestuffs are unsuitable. Good penetration depends largely on the correct choice of

dyestuffs, the desirable properties being slow exhaustion or very good levelling.

Dyeing has been well defined as "applied chemistry" and this—the third phase—is becoming more true every day. Modern dyeing demands of the present-day dyer an increasing knowledge of advanced organic, inorganic, and physical chemistry, whilst a well-equipped laboratory and chemical staff is absolutely necessary for the efficient running of the modern dyehouse. Not only should the dyer have an expert knowledge of the properties of the chemicals and dyestuffs used, together with a knowledge of the preparatory and finishing processes through which the material must pass, but he has also to have a sufficient training in chemistry to understand the chemical processes involved in the application of dyestuffs. The wide use of auxiliary products has made it necessary to appreciate why under certain circumstances a cation active product may be used, whilst in others an anion active or non-ionogenic body only is admissible, and why cation and anion active bodies should not be used together.

The statement has often been made that the dyestuff firms, with their constant flow of new dyestuffs, their technical service, and their sumptuous volumes of instructions together with the establishment of laboratories in the dyehouse, have depreciated the position of the foreman dyer. This is a very superficial view to take, because all the pattern cards and most detailed instructions issued can never give a person the requisite practical knowledge, without which no one can ever be a master or foreman dyer. Conditions vary with different dyehouses, and these have all to be studied by the foreman dyer in conjunction with the dyehouse chemist. The collaboration of the dyer and the dyehouse chemist undoubtedly produces better results than advice from the "expert," who is frequently taught more by the dyer than he teaches the dyer. An average person need only take a recipe out of a pattern card, go into a dyehouse, and attempt to get the same result. Such an attempt would prove disastrous and would serve to emphasize the necessity of leaving dyeing to the foreman dyer.

The fourth phase—the increasing number and variety of fabrics—is explained by two facts. The steady increase in the

varieties and quality of synthetic fibres, viz. viscose, acetate, cuprammonium rayons, staple fibres, casein fibre, staple fibre with affinity for wool dyestuffs, nylon and vinyon, coupled with their economic price and the increasing experience in blending and weaving these fibres in conjunction with other fibres has led to an ever widening use of these synthetic fibres in mixed goods. There appears to be no doubt that the future will see considerable expansion of these synthetic fibres, which will inevitably result in still further demands being made on the skill and resource of the dyer.

However much one may regret it, the ever-present demand for cheapness must always be recognized. Mass production in modern industry takes the form of a cheap, not a dear article, so that a constant endeavour is made by cloth designers to make as good an imitation as possible of a costly fabric in a cheaper material. This explains why one now meets so many fabrics which contain wool and cotton or staple fibre to imitate at a low price the more expensive all-wool article. These fabrics have naturally to be coloured, and this has led to the increasing demand for union dyestuffs which has been one of the most striking modern features in the coal-tar dyestuff industry. It will easily be understood that it is much more difficult to produce a good result on a wool and cotton fabric than a similar result on an all-woollen article, and such union fabrics, therefore, demand greater skill on the part of the dyer.

The final phase may be illustrated by reference to the demands for dyeings which will not only withstand the severe processes of milling, potting and cross-dyeing ; for dyeings able to withstand kier-boiling and bleaching, but also the new waterproofing, trubenizing, and crease resisting finishes. The production of such shades throws an added strain on the dyer, as a faulty dyeing may produce endless trouble in the subsequent stages of manufacture which may result in very heavy claims for damages. It should be pointed out that these trends are often mutually contradictory.

The introduction of viscose and acetate spun dyed rayons, *i.e.* shades produced by incorporating coloured pigments into the spinning solutions has, to some extent, relieved the dyer of producing the expensive shades required for effect threads and

has enabled the production of many shades at a cost and fastness hitherto unobtainable.

Of interest to all dyers is the legal judgment given in the *Griffiths* v. *Peter Conway, Ltd. Case* in 1938 and upheld in the Court of Appeal in 1939 on the question of a claim for damages due to dermatitis alleged to be caused by the wearing of a Harris tweed coat. This claim, like all others, was based on the Sale of Goods Act (1893), section 14, which may be summarized by saying that a textile fabric must be of merchantable quality and reasonably fit for the purpose for which it is sold. The legal question turned on whether "reasonably fit" covered the person who is idiosyncratic whilst thousands of other people were immune to a particular textile. The judgment in the case quoted above now established idiosyncrasy of the claimant as a defence in actions of this kind, but for this defence to succeed the idiosyncrasy must be clearly established and there must be no question of the garments themselves being injurious, *i.e.* due to their containing deleterious chemicals (see Whittaker, *J.S.D.C.*, 1938, p. 447; Bunbury, *ibid.*, 1939, p. 405).

Section II.—TEXTILE FIBRES: THEIR STRUCTURE AND IDENTIFICATION

THE textile fibres may be broadly classified into the following groups :

(a) Natural cellulosic fibres, such as cotton, linen, jute.

(b) Natural protein fibres, wool, and silk.

(c) Synthetic fibres on a cellulose basis, such as viscose rayon, acetate rayon, " Rayolanda " X.

(d) Synthetic fibres on a protein basis—casein fibre.

(e) 100 per cent. synthetic fibres, nylon, and vinyon.

(f) Mineral fibres, asbestos, and glass fibre.

The relative importance of the chief textile fibres may be seen from the following world production figures for 1930 and 1939 :

	1930 (1,000 lb.)	1939 (1,000 lb.)
Rayon yarn	451,200	1,147,280
Staple fibre	6,250	1,083,680
Cotton	12,400,000 ·	13,800,000
Wool (scoured basis)	2,220,000	2,420,000
Silk	130,000	104,000
	Average 1930/1934	
Flax ..	1,404,000	1,973,000 (estimated)

This table illustrates the enormous increase in the production of continuous filament rayon yarn and staple fibre, which has not been at the expense of cotton or wool, as their production has also increased at the same time.

In the case of the older textile fibres, such as cotton, silk wool, etc., adequate textbooks dealing with these fibres are available, so that in this section they are only briefly discussed. On the other hand, the available information relating to some of the fibres which are being developed at the present time, e.g. casein fibre, nylon, is widely scattered in the literature so that these fibres have received a more detailed treatment. As several textile fibres consist esentially of cellulose or cellulose derivatives

structure ; actually all that has been established is that parts of the cellulose have this structure since X-rays show that cellulose has a discontinuous crystalline structure. In other words, a cellulose fibre is not a single crystal, but a crystalline aggregate. The small crystals which build up the fibre are known as " crystallites " or " micelles " and the material between these crystalline areas as " intercrystalline material." The form and arrangement of the cellulose crystallite and its relation to the
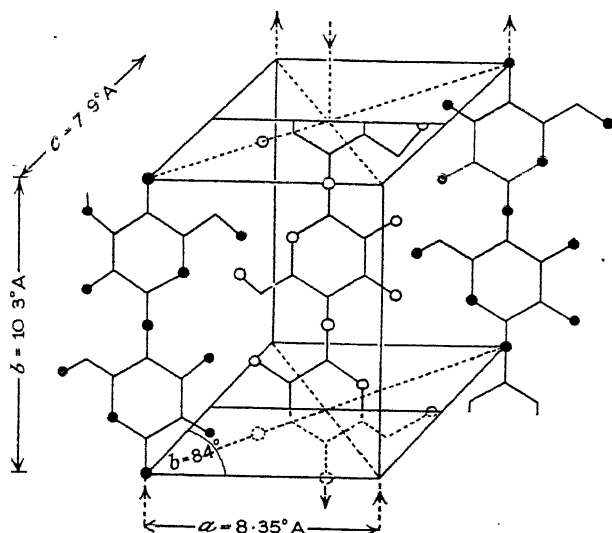
Representation of the monoclinic elementary cell of cellulose (according to Meyer and Misch). Three chains of glucose units are shown, running parallel to the *b* axis (fibre axis).

intercrystalline material has been and still is the subject of considerable discussion. Four theories have been suggested.

(*a*) *The Micellar Theory.*—This was put forward by Meyer and Mark (*Ber. B*61, 593, 1928) who consider that primary valence forces hold the glucose units together and secondary valence forces hold the chains alongside each other to form the micelle. Hengstenberg and Mark (*Z. Krist*, 69, 271, 1928) state that the estimated size of the micelle is 500 A° long and 50 A° thick. The micelles are considered to be held together by an amorphous cementing material in the manner that bricks held by mortar are used for building purposes. This theory has been abandoned in favour of the continuous structure theory.

(b) *The Continuous Structure Theory.*—Physical measurements indicate the molecular chains to be more than ten times the established size of the micelle, and this has led to the view that a single chain molecule may be a component of several " crystallites " (see Kratky and Mark (*Z. Phys. Chem.* 1937, 36B, p. 129)). The fine structure of cellulose is, therefore, probably best conceived as a three-dimensional network of more or less parallel chains which here and there fall into restricted regions of crystalline conformation.   In the fibre those regions possessing a definite crystalline regularity of cellulose chains may be considered as " crystallites " and where the chains have an irregular arrangement these areas may be considered " amorphous " or " intercrystalline " cellulose materials.   When such a structure is swollen by immersion in water osmotic forces tend to cause the chains to move apart, but in the crystalline regions this is prevented by crystal forces, so that between the crystallites, in the swollen condition, the molecular chains will form an open network through .which small molecules may pass with ease (Boulton, Delph, Fothergill, and Morton, *J. Text. Inst.* 1933, p. P113). The size of the pores in the intercrystalline regions of the water-swollen cellulose structure are about 20 A° (Morton, *Trans. Far. Soc.*, 1935, p. 262), the average dimensions of a direct cotton dyestuff molecule being about 30 $\times$ 8 $\times$ 3 A°.   As the crystallites are too closely packed to be penetrated by dyestuff molecules they must, therefore, be absorbed in the more or less individual molecular chains in the amorphous regions.   It is probable that there is a specific fraction of non-crystalline cellulose available for the fixation of dyestuff molecules characteristic of each variety of cellulose.   Thus, Morton (*ibid.*, 1935, p. 281) finds that, in the swollen state, all types of cellulosic fibres take up dyestuff from alcoholic solution, whereas in the unswollen state viscose rayon and mercerized cotton are unstained, whilst cuprammonium rayon and unmercerized cotton take up the dyestuff almost as easily as in the swollen condition.   In the unswollen state the cellulose in the former group of fibres possesses only very small capillary canals and, in the latter group, comparatively large canals, but not so large as to permit of rapid desorption of dyestuff.   These differences in fine structure have received little attention from investigators in this field.

(c) *The Cellulose Particle Theory.*—The original work (mainly microscopical) of Farr and Ekerson (contrib. *Boyce Thompson Inst.*, 6, 189, 309, 1934) and subsequent work by Farr (*J. Applied Phys.*, 8, 228, 1937) has led to the suggestion that the cellulose particle may be substituted for the micelle or crystallite. These particles which are ellipsoidal in shape ($1 \cdot 1 \mu$ thick and $1 \cdot 5 \mu$ long) exhibit all the properties of crystalline cellulose, and are covered with a coating of non-crystalline pectinous " cement." The assumption that these particles are the fundamental building units is based on the fact that they may be observed in the living cytoplasm of young cotton fibres. During fibre growth the particles unite end to end to form fibrils which are deposited in a spiral arrangement to build the mature cell wall. The natural fibre can be disintegrated into fibrils and these to particles by suitable solvents.

The evidence for the existence of such particles is doubtful, since it has been shown by Hock and Harris (*Am. Dyes. Rep.* 1940, p. 287), that particles may be seen when no cellulose is present in the cuprammonium solution used as the solvent. Again, Farr explains the viscosity of cellulose solutions in cuprammonium to the dissolution of the " cement," an explanation which does not appear to fit in with work on the viscosity of other polymeric materials.

(d) *Macromolecular Theory.*—As a result of the examination of a wide variety of synthetic polymeric substances of high molecular weight, Staudinger states that the presence of long narrow macromolecules, formed into bundles or crystallites by inter-molecular forces, are essential for the production of a useful fibre. These crystallites can exist only in the solid state or in very concentrated solution, since in dilute solution the inter-molecular forces are overcome by solution forces giving single macromolecules which are responsible for the viscosity of their solutions. Thus, in solutions which are not highly concentrated molecular colloids (*Ber.* 1929, p. 2893) are present which are colloidal in nature, but are different from micellar colloids which are built up from small independent molecules as with the soaps. The striking resemblances between the physical properties of cellulose and its derivatives, and those of the synthetic linear polymers of high molecular weight leaves little doubt that

cellulose is a linear polymer, so that the investigation of the synthetic polymers has provided strong evidence of the essential correctness of the linear structure assigned to cellulose.

THE NATURAL CELLULOSIC FIBRES

Cotton.—Raw cotton consists of the cellulosic hairy material which covers the seeds produced by the various species of the cotton plant (Gossypium). The dimensions of these hairs vary considerably, as may be seen from the following figures quoted by Marsh and Wood ("An Introduction to the Chemistry of Cellulose," 1938, p. 7) :

	Sea Island	*Egyptian*	*American*	*Indian*
Length (inches) ..	1·8–2·5	1·4–1·7	1·08–1·2	0·9–1·2
Fineness (inches) ..	1/1600	1/1500	1/1300	1/1200

The highest priced cotton is the Sea Island type, since its long staple and fineness enables the finest counts to be spun from it.

When examined under the microscope, cotton fibres are ribbon-like in appearance with convolutions or spiral twists, usually from left to right along their length. Cotton when freed from natural impurities consists of cellulose and is completely insoluble in water, alcohol, and other ordinary solvents. It is, however, soluble in cuprammonium solution, a property made use of in the fluidity test for assessing chemical damage of cellulose during processing. In this test, a 0·5 per cent. solution of cotton or a 2 per cent. solution of a regenerated cellulose rayon in cuprammonium solution is prepared and its viscosity determined under standard conditions. It has been shown that when the fluidity, *i.e.* the reciprocal of viscosity, of the solution is plotted against the extent of chemical tendering that the curve approximates to a straightl ine (see Farrow and Neale, *J.T.I.*, 1924, p. 157 ; Clibbens and Geake, *ibid.*, 1928, p. 77 ; " The Viscosity of Cellulose Solutions," 1932, H.M. Stationery Office). This method, therefore, serves to distinguish between chemical and mechanical damage of cellulose. Cotton is also soluble in benzyl methyl ammonium· hydroxide and cupri-ethylene diamine solutions.

Hot solutions of mild alkalies and alkaline salts such as soap, sodium carbonate, etc., do not degrade the cotton fibre, nor do

2

hot dilute solutions of caustic alkalies, such as caustic soda, providing air is excluded during treatment. In the presence of air the latter tenders the fibre due to the formation of oxycellulose, so that when pressure boiling cotton with caustic alkali it is essential to exclude air, or damage to the cotton will result. Strong solutions of caustic alkali, 20–25 per cent., swell cotton cold, a behaviour observed in 1844 by John Mercer, and subsequently patented by him in 1850 (B.P. 13,296). This, together with Lowe's discovery (B.P. 20,314 of 1889 and 4452 of 1890) that by maintaining cotton yarns under tension during the caustic soda treatment an increased lustre of the yarn is achieved, forms the basis of the treatment known as " mercerizing." In addition to its increased lustre, mercerized cotton has a greater affinity for dyestuffs, particularly if it is not dried before dyeing, and a higher strength than unmercerized cotton.

Dilute solutions of mineral acids and acid-producing salts, $c.g.$ Al_2Cl_6, $ZnCl_2$, have little action on the cotton fibre, providing they are well washed out before the fibre is dried. If this is not done hydrocellulose, a breakdown product of cellulose, is produced with consequent tendering of the cotton. Advantage is taken of this in carbonizing wool. Cold concentrated solutions of mineral acids swell cellulose and hot solutions hydrolyze it to give degradation products (cello-dextrins) which reduce Fehling's solution. Treatment with sulphuric acid of about 62 per cent. strength results in a mercerization-like effect and has enabled linen-like, wool-like, and transparent effects to be produced on cotton pieces ; the Heberlein Co. have been particularly active in this field. Most organic acids in dilute solution have little effect on cotton even when dried in, but oxalic, citric, and tartaric acids are exceptions and cause tendering. In strong solutions, particularly in presence of a catalyst, organic acids together with their anhydrides esterify cellulose giving products, which are usually soluble in organic solvents, such as acetone or chloroform. Such solutions are used for a variety of purposes, including the production of acetate rayon.

Under certain conditions, treatment of cotton with oxidizing agents such as potassium permanganate, sodium hypochlorite, etc., produce oxycellulose with accompanying tendering of the material. A considerable amount of work has been done on the

effect of hypochlorite on cotton as this is the usual method employed in cotton bleaching (see Clibbens and Ridge, *J.T.I.*, 1927, p. 135). The maximum production of oxycellulose is attained by treatment at $pH7$, and the least when the hypochlorite solution is definitely alkaline, so that in practice it is essential to ensure that all such bleach baths are kept alkaline, if necessary by the addition of sodium carbonate. The temperature of the solution should be as low as possible and direct sunlight should be avoided to ensure minimum oxycellulose production.

Linen.—Linen is manufactured from the bast fibres of the flax plant, Linium usitatissimum, which are separated from the ligneous portions by a process of retting or rotting. In the main, retting is a slow bacterial decomposition carried out in tanks or running water (water retting) or by exposure to atmospheric influences (dew retting).

The flax fibres vary considerably in length, the average length being about 20 inches. Although consisting essentially of cellulose it differs in physical properties from cotton in being built up of bundles of individual laminated tapering cells (or filaments) having lengths of 8–69 mm. and diameters of 0·0076–0·0305 mm. The strength of the flax fibre is considerably greater than that of cotton, but it is more easily injured by bleaching than the latter. This is not surprising, since the raw material contains approximately 20 per cent. of alkali soluble material in intimate relation, if not in actual combination, with the cellulose of the fibre, whereas cotton contains only about 5 per cent. of impurities. Again, unless carefully handled there is always the danger that linen yarns may become matted owing to the displacement by friction of some of the external filaments of the threads.

Jute.—Jute is a bast fibre obtained from the plants of the genus Corchorus by steeping the plant in water until the bark is sufficiently softened by retting (or rotting) to allow of separating the fibre by hand, using a beating process. The larger proportion of the world's jute supply is produced in North East India and is exported in bales in long fibrous masses, which require to be separated from sand, bark, and root portions before spinning into yarn.

The jute fibres, which may be $1\frac{1}{2}$–$2\frac{1}{2}$ yards long, consist of

bundles of single cells having lengths of 0·75–6·0 mm. and diameters of 0·0051–0·0254 mm. The modern conception of the jute fibre structure is that the main cellulosic part is a mixed crystalline structure of long chain cellulose aggregates and short chain xylans more or less perfectly oriented along the longitudinal axis of the fibre in steep spirals. This cellulosic part is encrusted with non-cellulosic materials such as lignin, whose constitution is unknown, and hemi-cellulose, which also serve to bind the cells together in the bundle. The xylans are polysaccharides built up of xylose units, linked in the same way as the glucose units in cellulose, but terminated at one end by an arabofuranose residue (see Haworth, *J.S.D.C.*, 1940, p. 53) : on hydrolysis they yield furfural :
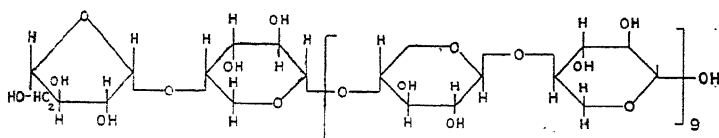
Xylan Structure.

Jute contains 12 per cent. flax and hemp 2 per cent., and cotton a negligible amount of xylan expressed on the weight of purified cellulose.

In yarn form jute is not as strong as cotton, and even water at ordinary temperatures tends to lower its strength. Hot caustic alkalies rapidly reduce the strength of jute, whilst cold concentrated alkalies swell it and cause a shrinkage in length, giving what is known as "woollenized" jute, which has been used as an adulterant for wool. Mineral acids readily attack the xylans and cause considerable deterioration, if dried in, whereas the volatile organic acids, such as acetic acid, are not dangerous.

A series of papers on the production and processing of jute were read at the British Association meeting in 1939 (see *J. Tex. Inst.*, No. 7, 1939).
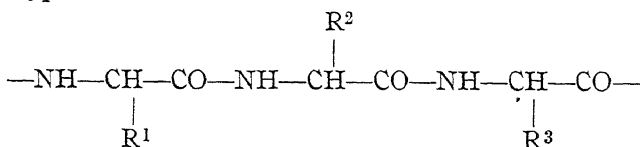
THE PROTEIN FIBRES

Wool.—Wool, the most important of the animal fibres, is strictly speaking, the hair of the sheep, but the hair of certain

goats, *e.g.* Mohair or Cashmere, and of the camel are usually associated with wool. Many varieties of wool are produced by different sheep, differing in length, diameter and other characteristics ; thus, wools may vary in fibre length from 1 in. to 8 in. or more, and in diameter from 0·001 in. to 0·008 in., the diameter usually being proportional to the length. Wools are, therefore, classified as long or short staple ; long staple wools being those above 1½ in. in length which are suitable for the spinning of worsted yarns, and short staple wools those which are less than 1½ in. in length, which are mainly used for spinning into woollen yarns. Under the miscroscope, wool is rod shaped in form, with surface scales all projecting in the same direction (see Plates   ).

Chemically wool, like hair, horn, and feathers, belong to that group of proteins known as the keratins. Mainly as a result of the work of Emil Fischer and others protein molecules are considered to be based on the repeated condensation of a-amino acids of the general formula NH_2—CH—COOH to form chains

$$\underset{\displaystyle R}{|}$$

of the type :

$$-NH-\underset{\displaystyle R^1}{\underset{|}{C}}H-CO-NH-\underset{\displaystyle R^2}{\overset{|}{C}}H-CO-NH-\underset{\displaystyle R^3}{\underset{|}{C}}H-CO-$$
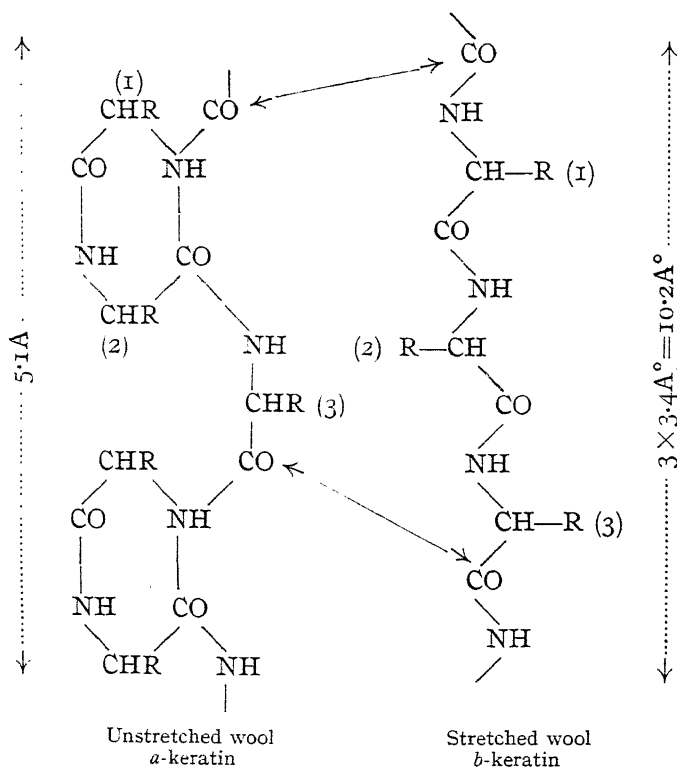
so that there is in proteins a sequence of amino-acid residues —NH—CH—CO linked at the peptide linkage CO—NH—from
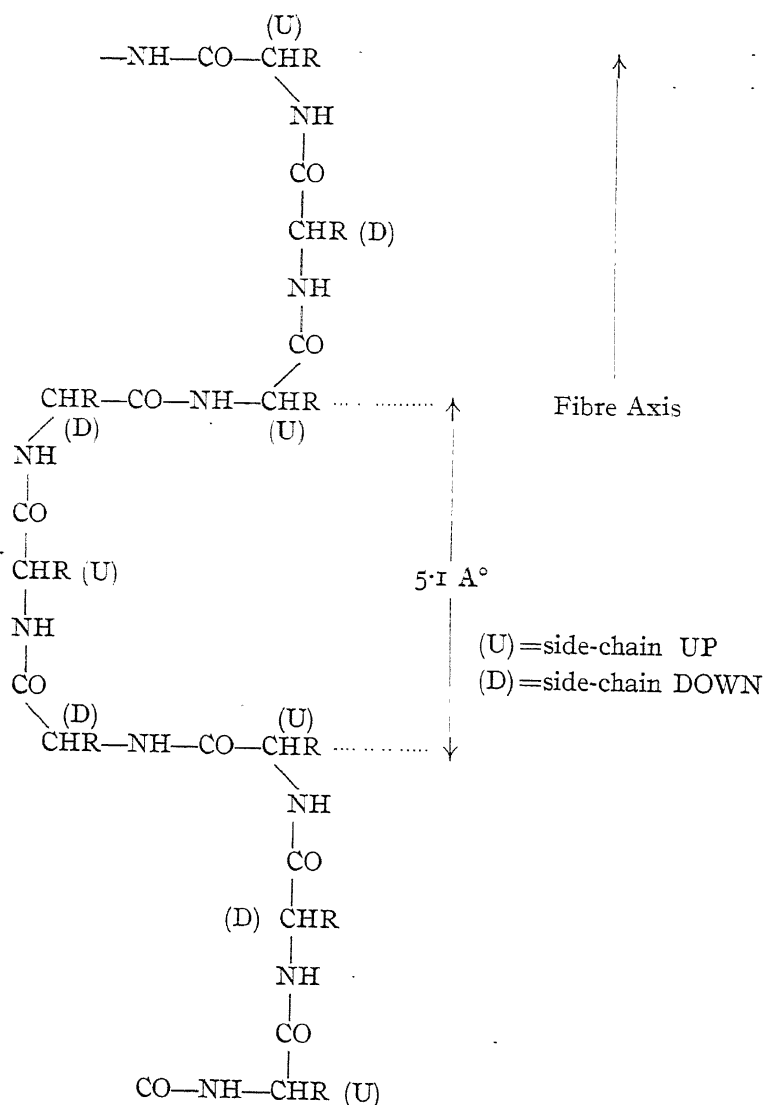
$$\underset{\displaystyle R}{|}$$

which the amino acids may be recovered by acid hydrolysis. The groups R^1, R^2, R^3 in the peptide chain represent hydrogens or side chains, some of which contain amino, carboxyl or sulphide groups, which may act as binding links between adjacent polypeptide chains. Meyer and Mark (*Ber.*, 1928, p. 1932) have shown that the length per amino acid residue, *i.e.* between R^1 and R^2, of a fully extended peptide chain should be of the order of 3·5 A°. X-ray analysis has shown that with unstretched wool keratin the period is 5·1 A° which does not correspond with any period in the straight chain. Wool, however, will stretch to

double its length without tearing, and with stretched wool the period 3·4 A° is found.

Astbury and Woods ("Nature," 1930, p. 913) considered that in unstretched wool the chains are coiled up into hexagons which on stretching the fibre are opened up thus :

```
                                          \
  ↑                               ⟶        CO          ↑
        (1)         |                     /
        CHR    CO ⟵                      NH
       /       \                          \
      CO        NH                          CH—R (1)
      |         |                          /
                                          CO
      NH        CO                          \
       \       /                             NH
        CHR                                 /
        (2)         NH         (2) R—CH
                    |                      \
                    CHR (3)                 CO
                                           /
        CHR         CO ⟵                  NH
       /       \                            \
      CO        NH                            CH—R (3)
      |         |                           /
                                           CO
      NH        CO                           \
       \       /     \                        NH
        CHR    NH                            /
               |
```

5·1A (left vertical dimension)   3×3·4A°.=10·2A° (right vertical dimension)

| Unstretched wool | Stretched wool |
| a-keratin | b-keratin |

Evidence has been accumulated, in particular from the experiments of Neurath (*J. Phys. Chem.*, 1940, p. 296), which shows that there is no room for the side chains when the main chains are folded in this way. Astbury and Bell ("Nature," 1941, p. 696 ; see also Astbury "Chemistry and Industry," 1941, p. 494) as a result of this evidence have suggested that the nature of the fold is as follows :

(U)

—NH—CO—CHR

        \
        NH

        |
        CO

        |
        CHR (D)

        |
        NH

        |
        CO

        /
CHR—CO—NH—CHR ⋯ ⋯⋯⋯↑   Fibre Axis

/ (D)   (U)

NH

|
CO

|
CHR (U)

|
NH   5·1 A°

|
CO   (U)=side-chain UP

\ (D)   (U)   (D)=side-chain DOWN

CHR—NH—CO—CHR ⋯⋯⋯↓

        \
        NH

        |
        CO

        |
(D) CHR

        |
        NH

        |
        CO

        |
CO—NH—CHR (U)

No complete amino acid analysis of any protein has yet been realized; with wool a complex mixture of amino acid radicals, including arginine, lysine, cystine, aspartic acid, glutamic acid, is obtained on acid hydrolysis. Arginine and lysine give rise to positively charged centres, whilst with cystine the sulphur atom

can pass reversibly into either the disulphide or hydrosulphide form. In the wool fibre, therefore, bridging may arise by the formation of these types of chemical linkage ; electrostatic or salt links between the positively and negatively charged centres of certain side chains ; co-valent links between adjacent sulphur atoms forming a disulphide bridge ; co-ordinate links between the adjacent carbonyl and imino groups at the peptide links of adjacent backbones where they come sufficiently close together ; of these, the disulphide bond (cystine linkage) is probably the most important.

The presence of both acid and basic groups in the wool molecule is responsible for the affinity of the fibre for basic and acid dyestuffs respectively, according to whether the pH is higher or lower than the isoelectric point of 4·8.

The bridging of the peptide chain may be represented as on next page.

Wool when treated with boiling water, or when steamed, swells and has an increased affinity for most dyestuffs, and when treated under tension or pressure acquires a permanent set which reduces the formation of creases in dyed wool piece goods.

Compared with water, dilute acids have little further effect on wool, but are absorbed and retained by the fibre with great tenacity. The combination of acids with wool is stoichiometric and 100 gms. of dry wool are capable of combining with 80 cc. N/1 hydrochloric acid which is largely accounted for by the free amino groups in wool formed as result of breakdown of the salt linkages (see Speakman, *J.S.D.C.*, 1933, p. 180). Boiling moderately strong acid solutions, *e.g.* 20 per cent. HCl, hydrolyze wool giving a complex mixture of amino acids, whilst cold concentrated mineral acids completely destroy and dissolve the fibre.

Dilute solutions of caustic alkalies rapidly disintegrate wool at a rate depending upon the temperature and concentration employed. This property forms the basis of the extraction of wool in admixture with cellulosic fibres, the material being weighed before and after treatment with a 10 per cent. solution of caustic soda at the boil, which dissolves out the wool and leaves behind the cellulosic fibre. Cold, very strong (80° Tw.) caustic soda

$$
\begin{array}{c}
\diagup CO \\
-CH \diagdown \\
\diagup NH \\
CO \diagdown \\
\diagdown CH \text{———} CH_2-S-S-CH_2 \text{———} CH \diagdown \\
NH \diagup \\
\diagup CO \diagdown \\
-CH \diagup \\
\diagdown NH \\
\end{array}
$$

cystine linkage

glutamic acid   lysine

$CH-CH_2-CH_2-\overline{COO} \quad \overset{+}{NH_3}-CH_2-CH_2-CH_2-CH_2-CH_2- CH-$

aspartic acid   arginine

$CH \text{———} CH_2-\overline{COO} \quad \overset{+}{NH_3}-C-NH-CH_2-CH_2-CH_2 \text{———} CH$

$\overset{\parallel}{NH}$

salt linkages
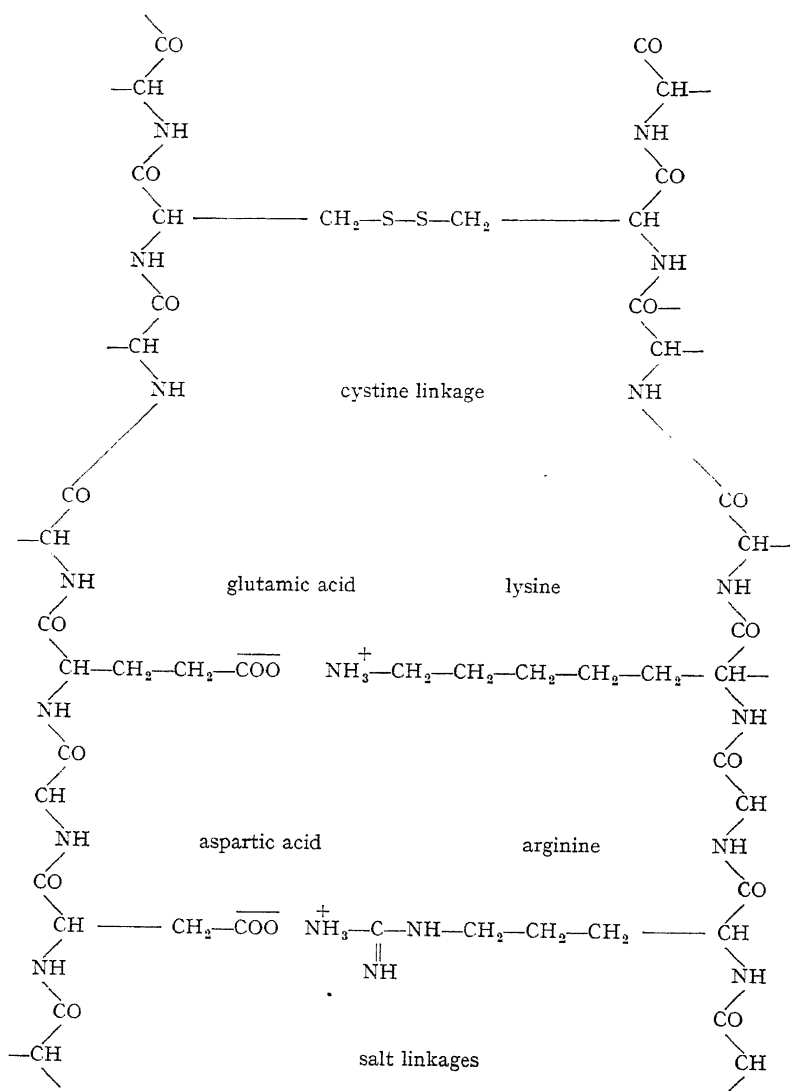
solution increases the strength of wool and gives to it an increased affinity for dyestuffs (see Matthews, *J. Soc. Chem. Ind.*, 1902, p. 685). Alkaline carbonates have a much less destructive action on wool and when used in dilute solutions as in wool scouring no injurious effect is observed ; borax, soap, and ammonia behave similarly.

When wool fabrics are submitted to the combined action of soap liquors and friction (see Milling) they become thicker and shrink in length and width, *i.e.* they felt. A similar, though less drastic, alteration in dimensions occurs when wool garments (underwear, socks, etc.) are repeatedly washed so that finally the garments become too small for their original purpose. Several processes for rendering wool non-shrinking, based on treatment with liquors containing or capable of liberating active chlorine or hypochlorous acid have been used during the last forty years. For example, the wet yarn is treated in a Hussong machine with cold $\frac{3}{4}°$ Tw. sodium hypochlorite for $\frac{1}{2}$ hour, 6 per cent. hydrochloric acid 30° Tw. gradually added, the treatment continued for $\frac{1}{2}$ hour and the yarn finally well rinsed. Alternatively the yarn is first treated with acid, drained or lightly hydro-extracted, treated with hypochlorite and again with acid. Such solutions are stated to prevent felting, giving a less durable wool, whilst these processes, unless carefully controlled will give variable results. In order to minimize these defects the use of solutions of bromine instead of chlorine has been suggested, whilst Clayton and Edwards (E.P. 537,671) have suggested the use of hypochlorous acid, chlorine or bromine in presence of an organic acid having reducing properties, *e.g.* formic or lactic acid. Again Meunier and Latreille (*Chim. et Ind.*, 1923, p. 636) use gaseous chlorine to produce unshrinkable wool without appreciable damage to the wool, a principle which has been revived with the use of special apparatus to give more accurate control of the process by the Wool Industries Research Association (E.P. 417, 719, and E.P. 275, 742). More recently Hall, Hicking, and Pentecost (E.P. 464, 503) have developed the Dri-Sol process, which uses a $1\frac{1}{2}$–2 per cent. (by volume) solution of sulphuryl chloride in white spirit at 15° C. When using either the chlorine gas or the sulphuryl chloride process it is essential to control the moisture content of the wool to prevent localized damage.

It has been known for many years (Schneider E.P. 11,834 of 1908) that treatment of wool with caustic soda solutions below 32° Tw. at ordinary temperatures makes wool non-shrinking, but this process does not appear to have been used commercially. Interest in the use of caustic soda and other alkalies for this

purpose appears to have been revived since Tootal Broadhurst Lee Co., Hall and Wood (E.P. 538,396, 538,428) suggested the use of alkalies in organic liquids (methyl or ethyl alcohol, or mixed solvents) containing little or no water to render wool non-shrinking. Work on this subject has also been described by Freney and Lipson (Council for Scientific and Industrial Research Australia, Pamphlet No. 94, 1940).

A new method for rendering wool non-shrinking involving the use of the enzyme papain in presence of sodium bisulphite at pH 6·65, and at 65° C. is also in process of development. (Wool Industries Research Association, Phillips and Middlebrook, E.P. 513,919 ; see also *J.S.D.C.*, 1941, p. 137). Wool treated by any of the above non-shrinking processes has an increased affinity for acid dyestuffs.

Silk.—Silk is an animal fibre formed by the coagulation of a secretion from the spinning gland of the silk worm and consists of two parallel filaments cemented together with silk gum. Raw silk fibres consist of two proteins, silk fibroin ($C_{15}H_{23}N_5O_6$) and silk sericin ($C_{15}H_{25}N_5O_8$) known also as silk gum which forms a coating over the fibroin, the latter constitutes about 20 per cent. of the total weight of the raw silk. Like wool, silk fibroin consists of peptide chains lying parallel, X-ray analysis showing evidence of a periodic repetition of structure at a distance of 7·0 A° which corresponds with the distance calculated on the assumption that the chains are straight, thus :

$$-NH_2-CH_2-CO-NH-CH-CO-NH-CH_2-CO-NH-CH-CO-$$
$$CH_3 \cdots \cdots 7 \cdot 0 \, A° \cdots \cdots CH_3$$
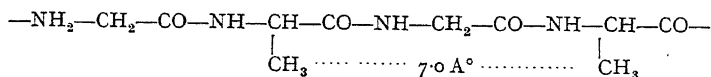
It should be noted that silk has none of the cross-linkages characteristic of wool. In its behaviour with acids silk is somewhat like wool, except that it is more readily attacked by strong acids. On the other hand, it is rather more resistant to all alkalies, except caustic soda and caustic potash.

Silk may be dissolved in cupri-ethylene diamine solution which makes it possible to determine the fluidity of silk solutions and to investigate any chemical damage suffered by silk during processing (*J. Text Inst.*, 1941, p. T1).

SYNTHETIC FIBRES ON A CELLULOSIC BASIS

These fibres can be divided into three groups, thus :

(a) *Regenerated Cellulose Rayons.*—The fibres under this heading include continuous filament rayons (viscose, cuprammonium and nitro), viscose staple fibre (viscose " Fibro ") and the more recently developed strong viscose yarns (" Tenasco "). Many textbooks dealing with the manufacture of these fibres are available (see Bibliography), to which the interested reader is referred. As regards strong viscose yarns, these are produced by the ordinary viscose spinning process using stretch spinning conditions chosen to give a dry tenacity considerably higher than normal viscose rayons (Rose, *J. Text. Inst.*, 1939, p. P202).

Regenerated cellulose rayons have a lower wet and dry strength than cotton and require to be carefully handled, particularly when wet, to avoid mechanical damage to the filaments. With acids, alkalies, etc., they re-act in a manner similar to cotton, although in many cases much more readily.

(b) *Cellulose Acetate Rayons.*—For methods of manufacture, see textbooks in Bibliography.

Cellulose acetate rayon is also available in cut lengths (staple fibre) whilst more recently strong yarns, *e.g.* Celanese Forte, have been developed by a special stretch spinning technique.

This type of rayon is soluble in a wide variety of solvents, including acetone, chloroform, glacial acetic acid, but is insoluble in such solvents as benzene, petrol, ether, white spirit. On treatment with boiling water, and particularly with soap solutions alone or containing small quantities of phenol (Atkinson, *J.S.D.C.*, 1931, p. 5) or cyclohexanol it is delustred. It can, however, be boiled in strong salt solutions without loss of lustre. Cellulose acetate rayon is less readily attacked by dilute acids and oxidizing agents than are the cellulosic fibres, but it is readily attacked (saponified) by hot dilute solutions of alkaline carbonates, phosphates, hydroxides, etc., with loss in strength and weight, whilst at the same time acquiring an affinity for direct cotton and other dyestuffs which it did not previously possess.

(c) *Animalized or Basified Cellulosic Fibres.*—For many years attempts were made to " animalize " vegetable fibres mainly

with the idea of explaining the differences in dyeing properties of the animal and vegetable fibres. The first idea of animalizing cotton appears to be the suggestion of Thomas Henry (*Mem. Manchester Lit. & Phil. Soc.*, 1790) that the preparation given to cotton for dyeing of Turkey Red might give the cotton analogous qualities to those of animal fibres. Hermstadt (Berlin 1802) proposed to treat cotton with solutions of white of egg, milk, blood, glue, whilst Mueller-Jacobs (Textile Colourist, 1884) treated it with albumen and casein. Kuhlmann (*Compt. rend.* 1856) nitrated the cotton with a mixture of nitric and sulphuric acids, and Vignon (*Compt. rend.* 1890, p. 286, 909) treated cotton in sealed tubes for long periods at 100°–200° C. with ammoniacal calcium chloride and ammonia, when the cotton had the property of dyeing in an acid dyebath with Naphthol Black, Rocelline, etc.

During the past few years this problem has been extensively examined from a more practical point of view, viz : the production of wool substitutes in order to develop economic nationalism : also to produce fibres having useful and distinctive characteristics of their own. From the patent literature, work on this subject appears to be in progress on the following general lines :

(*a*) The application to staple fibre of quaternary ammonium compounds, or of components capable of forming nitrogenous condensation products on heating. By the treatment with quaternary ammonium compounds the long chain cations are absorbed on the fibre and form a lake with negatively charged dyestuff acid anion. Although the treated fibre has a very strong affinity for wool dyestuffs, the resulting shades are, in general, of poor fastness to light, washing and rubbing, with the exception of certain chrome shades which are of very good fastness to washing, but not to rubbing, so that no process based on this method has, as yet, been commercialized. A typical example of this type of treatment uses octadecylpyridinium bromide mixed with a caustic alkali solution of resin (Courtaulds, Ltd., Whittaker and Wilcock, E.P., 501,020).

(*b*) More success has been attained by the treatment of staple fibre with condensation products which led to the commercial production of " Artilana " in Germany and " Rayo-

landa '' in this country. In general, these processes involve a treatment with a solution of a condensation product or its components, followed by drying and treatment at a fairly high temperature to promote reaction.   Formaldehyde, together with a base, features in some of the patented processes, and probably under heat treatment reacts with the hydroxyl groups in the glucopyranose units of the cellulose chain to give methylene cross-linkages.   According to Barnes (*Text Col.*, 1937, p. 391), " Artilana," which has very little affinity for wool dyestuffs, consists of viscose treated before and after spinning with the components of a synthetic resin of the urea-formaldehyde type, following by crimping and subsequent resin formation to fix the crimp.   " Rayolanda," unlike " Artilana," has a good affinity for wool dyestuffs and possesses unique properties which justify its introduction as a new, and not as a substitute fibre.

The diversity of substances patented as basifying agents for cellulose is enormous and includes p-chloraniline (E.P., 504,572) melamine (E.P., 482,409), chloracetamide and pyridine (523,081), etc., used in conjunction with formaldehyde.   Yet in spite of this great patenting activity the only fibre commercially produced which will dye satisfactorily with a wide variety of wool dyestuffs is " Rayolanda."

(c) The incorporation of proteins, or nitrogenous condensation products into rayon spinning solutions has also been proposed, the greatest measure of success with such fibres having been reached in Italy with Cisalfa and in Belgium with Fibramine. Both of these products contain about $4\frac{1}{2}$ per cent. casein dispersed in viscose rayon.   According to Ferretti (E.P., 483,731 ; 483,809/10) alkaline casein solution is added to the cellulose xanthate spinning solution which is then extruded into an acid coagulating bath.   These fibres, particularly as regards their dyeing properties, much more nearly resemble viscose rayon than wool (Bunbury, *J. Text. Inst.*, 1939, p. P175), and have a somewhat lower tensile strength than the former.

The only fibre incorporating a nitrogenous condensation product in the spinning solution which has been marketed is " Vistralan " produced in Germany by the I.G.   In its production the compound obtained by reacting carbon bisulphide with ethylene imine is obtained as a finely divided powder which is

then dispersed in the cellulose xanthate solution (E.P. 493,509). This fibre possesses similar physical and dyeing properties to viscose rayon together with a good affinity for wool dyestuffs not possessed by the latter fibre. Like all other basified synthetic fibres it does not possess exactly the same dyeing properties as wool, so that when admixed with wool careful selection of dye-stuffs must be made to obtain satisfactory dyeings.

Synthetic Fibres on a Protein Basis

So far, using casein as the raw material, more technical and commercial success has been achieved with this than with any other protein fibre. Various other proteins have been suggested as suitable for the production of fibres, including Soya bean proteins (*Rayon Text. Monthly*, 1939, p. 53 ; *Ind. Eng. Chem.* 1940, p. 1549), Chitin (von Weimarn, *Kolloid Z.*, 1926, p. 120) ; Zein, the protein of maize (E.P. 492,623) ; globulins (Chibnall, Bailey, and Astbury (E.P. 467,704 ; 467,812), peanuts (E.P. 524,090), etc., but commercial development in this field appears to be confined to the use of Soya bean protein in the U.S.A.

Casein Fibre.—As long ago as 1898, Millar (E.P. 6700) pro-posed to use solutions of casein in acetic acid for the production of fibres, whilst in 1904 Todtenhaupt (E.P. 25,296) patented the spinning of a casein fibre from a solution in alkali. It was not, however, until 1935 when Comm. Antonio Ferretti patented (E.P. 483,731) a process concerned mainly with isolation and solution of the casein for the production of a synthetic wool-like fibre from casein known as " Lanital " that interest was revived in such fibres and they were produced commercially. The Ferretti process has been worked in Italy by the Snia Viscosa Co. at Milan and many others have acquired operating licences ; in this country a licence is held by Courtaulds, Ltd., the fibre being known as Casein Fibre. In America the only casein fibre patents granted are those held by Whittier and Gould (U.S.P. 2,140,274 ; 2,167,202 ; 2,169,690 ; *Amer. Dyestuff Rep.* 1939, p. 641 ; *Ind. Eng. Chem.* 1940, p. 906) which differ from Ferretti's patents in the constitution of the spinning solution and the precipitating bath.

In the manufacture of casein fibre the casein is first separated from skim milk by precipitation with mineral acids at pH 4,

and the dried product made into a colloidal solution using dilute caustic soda. This alkaline solution is then extruded into an acid coagulating bath (or baths) containing formaldehyde and aluminium salts which render the casein fibre insoluble and resistant to textile processes. The fibres are then cut into short lengths corresponding to the staple of natural wool, so that they can be worked in wool spinning processes. According to Diamond and Wormell (*J. Text. Inst.*, 1939, p. P.224) casein particles after coagulation and solution in alkali are largely denatured and are rod-like in shape. During spinning they tend to become oriented and the formaldehyde and aluminium salts form cross-linkages between the rods. It is suggested that the action of the form-aldehyde is to form a methylene link by joining up two amino-groups with loss of water thus :

$$-NH_2 + CH_2O = -NH-CH_2-OH$$
$$-NH-CH_2-OH + NH_2- = -NH-CH_2-NH- + H_2O$$
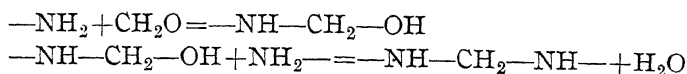
The methylene group is analogous to the cystine link, $-S-S-$ in wool. These authors consider that aluminium atoms unite with the acid carboxyl groups of the casein molecules, and so form a connecting link between the protein chains. Although, chemically, casein fibre bears a close resemblance to wool, the chief difference being the lower sulphur content, it differs con-siderably in its physical properties. It has a more or less " woolly " handle and similar heat-retaining properties to wool, but does not possess the same elastic recovery properties, especially when wet, and has a lower dry and a much lower wet strength. Unlike wool, casein fibre does not possess any felting properties, which is not surprising since it has a smooth surface in contrast to the scaly structure of wool. When used as a blend with wool it assists the felting of the wool, which accounts for its use in the hat trade, where use is made of up to 25 per cent. casein fibre admixed with wool noils to produce felt hoods. It is suggested that the casein fibres adhere to the wool fibres in the wet state and shrink more than the wool fibres (Thomas, *Chem· & Ind.*, 1939, p. 709). In warm soap solutions, casein fibre sorbs alkali and becomes plastic so that at the present stage of its development its use should be confined to outerwear. For the dyeing of casein fibre alone and in admixture, see Section 14.

100 PER CENT. SYNTHETIC FIBRES

There are, at the present time, two fibres now in commercial production which may be classified under this heading, viz. Nylon (formerly Fibre 66) and Vinyon. These fibres are thermo-plastic bodies, *i.e.* they can be softened and re-softened indefinitely by the application of heat and pressure. Their production is undoubtedly the result of earlier academic researches on the chemistry of long-chain polymers. The possibilities in this field of plastic chemistry are enormous, and it is safe to assert that fibres of this type will feature largely in the future developments of the textile industry.

Nylon.—The discovery of the nylons, the generic name for all synthetic fibre forming polyamides, was announced by E. I. du Pont de Nemours & Co. in 1938. These fibres, resulting from the fundamental work of W. H. Carothers and his co-workers, are superpolyamides prepared from the product of condensation of dibasic acids (*e.g.* sebasic or adipic acid) with diamines (*e.g.* penta or hexamethylene-diamine). Thus, sebasic acid and penta-methylene-diamine react to give a long chain polymer of the type represented by $(-CO-(CH_2)_8-CO-NH-(CH_2)_5-NH-)$. The condensation product is first made by heating the reactants in an autoclave under pressure, usually in an atmosphere of nitrogen to prevent oxidation, and then continuing the heating at a higher temperature in order to bring about polymerization. When the melt has attained the desired viscosity the molten polymer is extruded as a ribbon and ground. In this granular condition it is completely stable and may be stored for any length of time before spinning. In spinning the granular material is melted, extruded from a spinneret, or drawn, and the re-solidified filaments collected. As spinning temperatures of $10°-15°$ above the melting-point of the polymer are usually employed there is a tendency to undergo further polymerization, so giving non-uniform products. To overcome this, a viscosity stabilizer is added. This may be a monofunctional amide or amide-forming compound which prevents further polymerization by combining with the end group of the polymer chain analogous to the way in which a radicle is." blocked " in organic syntheses (see E.P. 495,790). The filaments are then cold drawn to approximately four times

3

their original length, thus orienting the long chain molecules and giving a very pronounced increase in the mechanical strength and elasticity of the nylon.

Nylon is somewhat similar to real silk in its appearance and fineness of denier. Its outstanding property is its tensile strength (5 gm./denier dry ; 4·4 gm./denier wet) which is greater than silk, and twice that of dry rayon increasing to three or four times against wet rayon. Again, the fibre elasticity and fabric elasticity (especially after steam setting, see below) is equal to or better than silk, *e.g.* with a 25 per cent. stretch at 85 per cent. R.H. the elastic recovery is 77 per cent. compared with 65 per cent. for silk yarn. It is less hygroscopic than all natural and synthetic fibres, *e.g.* the moisture content on a dry basis at 70 per cent. R.H. is 4·55 per cent. The melting-point of nylon is given as between 243° C. and 260° C.

Nylon has a high resistance to many chemicals, including acetic acid, hydrogen peroxide and sodium hypochlorite. On the other hand, boiling in 5 per cent. hydrochloric acid makes it brittle and finally destroys the fibres. It is soluble at 25° C. in phenol, m-cresol, xylenol and formic acid, whilst at high temperatures 80 per cent. acetic acid, also acts as a solvent. A notable property of nylon is that hot water or steam imparts a substantially permanent set to yarn and fabrics, *i.e.* if a fabric is smooth when treated, its tendency is to remain so. Once a nylon fabric has become set a condition of heat and moisture more severe than the conditions of set is necessary in order to effect a re-setting in another shape. Advantage is taken of this property in setting nylon stockings so that repeated wear and washing will not alter their original shape. The stockings are, therefore, " preboarded " in the desired shape immediately after knitting.

Vinyon.—This is a synthetic fibre derived from a vinyl resin, a co-polymerization product of vinyl chloride and vinyl acetate. When equivalent amounts of each component are mixed the structure of the co-polymer may be pictured as a long chain, the alternate links of which are vinyl chloride and vinyl acetate units thus :

$$-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-$$
$$\quad\; |\qquad\qquad |\qquad\qquad |\qquad\qquad |$$
$$O.COCH_3\quad\; Cl\qquad O.CO.CH_3\quad\; Cl$$
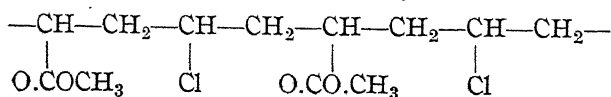
Of the various polymers that can be prepared, those having about 85–90 per cent. by weight of vinyl chloride are specially suitable for making synthetic fibres (see Bonnet, *Amer. Dye Rep.*, 1940, p. 547).

In producing yarns, the co-polymer is dissolved in acetone and spun in hot air, as is cellulose acetate rayon. This spun yarn is not strong, but after stretching several hundred per cent., may attain a strength of 1–4 gms. per denier. After stretching, the yarn is given a set by heating it under tension to 85°–100° C. which stabilizes the yarn in regard to shrinkage up to 65° C. ; if heated above this temperature shrinkage occurs.

Vinyon is unaffected by concentrated acids, 30 per cent. caustic soda solutions, alcohol, glycols, etc., but dissolves in acetone and may partially dissolve in or swell in certain esters, amines, aromatic hydrocarbons, etc. It does not absorb water in any appreciable amounts, but can be dyed with insoluble acetate dyestuffs in presence of small amounts of assistants, such as o-hydroxydiphenyl, etc. At present its largest use is in the manufacture of industrial filter cloths, whilst successful trials have also been made with Vinyon fish nets and lines, also gloves.

Mineral Fibres

These fibres are not of particular interest to dyers, but have their own specialized uses. Interest has recently been shown in the glass fibres, and the reader is referred to articles by Lindsay Forster (*J. Text. Inst.*, 1939, p. P162) and Bateson (*Chem. and Ind.*, 1941, p. 341).

Identification of Textile Fibres

The problem of fibre identification has resulted in the publication of numerous tests for this purpose which may be roughly classified as :

(a) Burning tests.
(b) Microscopic tests.
(c) Solubility and swelling tests.
(d) Staining and colour change tests.

Several schemes for the identification of textile fibres based on these tests have been suggested, but no scheme however detailed

can be said to eliminate completely the necessity for actual practice and experience in identifying the increasing number of fibres used in textile manufacture. Difficulties may arise when examining blends of different fibres, dyed fibres, or fibres from cloths which have received one of the modern finishing treatments, which may lead to wrong conclusions by the inexperienced. Nevertheless, with a little experience the following procedure, although not fully comprehensive, has proved satisfactory for normal dyehouse laboratory requirements.

Burning Tests.—A burning test of the fibres to be identified should be made, as this serves to give a general idea of the type of fibre which is present. In carrying out this test a strand of similar fibres is held over a small flame. If a mixture of fibres is suspected the individual fibres should be tested separately since a small percentage of one fibre may completely mask the presence of the other. The indications given by this test are shown in the following table.

Rate of burning	*Odour*	*Ash*	*Fibre*
None	None	None	Asbestos, glass fibre
Slow	Burning hair	Black bead	Protein fibre (wool, silk, casein fibre)
Slow	Burning hair	Grey ash, shape of original fibre	Protein fibre (weighted silk)
Rapid	Burning paper	Little or none	Cellulosic fibre (cotton, linen and other vegetable fibres ; rayons, except cellulose acetate ; basified rayons)
Rapid	Acrid, slightly aromatic	Hard black bead	Acetate rayon
None : melts	Little	Round ball	Nylon
None : melts	None	Irregular bead	Vinyon

Tests for Protein Fibres.—The presence of individual protein fibres may be confirmed as follows :

Reagent	*Wool*	*Silk*	*Casein fibre*
Cold concentrated hydro-chloric acid for 15 minutes	Insoluble	Soluble	Insoluble
30% soln. caustic soda for 3 hours at 30° C.	Soluble	Soluble	Insoluble
Fibre thoroughly wetted with water, immersed in cold Shirlastain A for 1 minute and washed	Bright golden Yellow	Raw silk : very dark brown. De-gummed : slightly brownish-orange	Yellow Orange

To distinguish between unweighted and tin-weighted silk the fibres are boiled with a little Alizarine Orange paste (C.I. 1033). Tin-weighted silk is coloured a bright orange, whereas unweighted silk is only stained a dull bluish-pink. A further test is to boil the silk with Logwood and acetic acid : tin-weighted silk is coloured violet, whilst unweighted silk is stained red.

Casein fibre may be identified in blends with wool by Whittaker's test (*J.S.D.C.*, 1937, p. 468). Thus, if wool and casein fibre are immersed for 1 minute in a cold solution of 0·5 gm. of certain wool dyestuffs and 0·5 c.c. 80 per cent. sulphuric acid per 100 c.c. water, and the material then rinsed it will be found that the casein fibre is dyed a full shade whilst the wool is only slightly stained. Suitable wool dyestuffs are Xylene Light Yellow 2G (C.I. 639), Azo Geranine 2GS (C.I. 31) and Erio Fast Cyanine S conc. (C.I. 1054). If a dyed fabric of wool and casein fibre is stained in this manner with a wool dyestuff of contrasting shade to the shade of the dyed fabric under examination, the relative distribution of the two fibres in the fabric can be seen either with the naked eye or under a microscope. This test is equally effective if the wool has been chlorinated.

Tests for Cellulosic Fibres.—The presence of individual cellulosic fibres may be confirmed by the following tests. With dyed samples it is only possible to carry out most of these tests after removal of dyestuff from the fibre by the methods indicated in Section XIII. In all cases when stripping has been employed the fibres must be extremely well washed with water before applying the test.

Reagent	Scoured cotton	Bleached linen	Mercerized cotton	Viscose rayon	Cuprammonium rayon	" Rayolanda" X
Fibre wetted with water, immersed in cold Shirlastain A for 1 minute and washed	Lilac	Violet blue	Purple	Bright pink	Bright blue	Brownish orange
$ZnCl_2$—I_2 solution	No colour	No colour	Blue	Blue	Blue	Blue
Whittaker's test (see above)	Undyed	Undyed	Undyed	Undyed	Undyed	Dyed

The $ZnCl_2$—I_2 solution is prepared by mixing 20 c.c. solution. A (280 grms. $ZnCl_2$ in 300 c.c. water) and 0·2 c.c. solution " B " (20 gms. KI in 100 c.c. water+1·0 gm. I_2).

Viscose and cuprammonium rayons can be distinguished by taking a little of the rayon under test together with known samples of viscose and cuprammonium rayons, and dyeing the fibres together in a cold dyebath containing a direct cotton dyestuff, preferably one with a high time of half-dyeing (Section XIII.), like Diphenyl Fast Blue Green BL, for 2 minutes with a little common salt. Cuprammonium rayon will be heavily dyed, whilst viscose rayon will only be tinted.

The little-used nitro-cellulose silk may be detected by the diphenylamine test : a small portion of the sample is dissolved in pure concentrated sulphuric acid to which has been added a trace· of diphenylamine. Nitro-cellulose silks give a bright blue colour immediately, whilst the other cellulose silks give only a slight yellow colouration.

Tests for Acetate Rayon, Nylon, Vinyon.—The presence of any of these fibres may be confirmed as follows :—

Reagent	Acetate	Nylon	Vinyon
Acetone	Soluble	Insoluble	Soluble
Glacial acetic acid (cold) ..	Soluble	Insoluble	Insoluble
90% phenol	Insoluble	Soluble	Insoluble
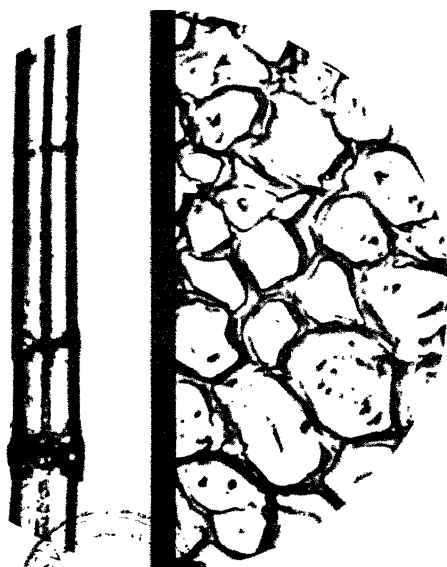
PLATE I

Linen.   ×500.

Cotton.   ×500.

PLATE 2

Viscose.   × 500.
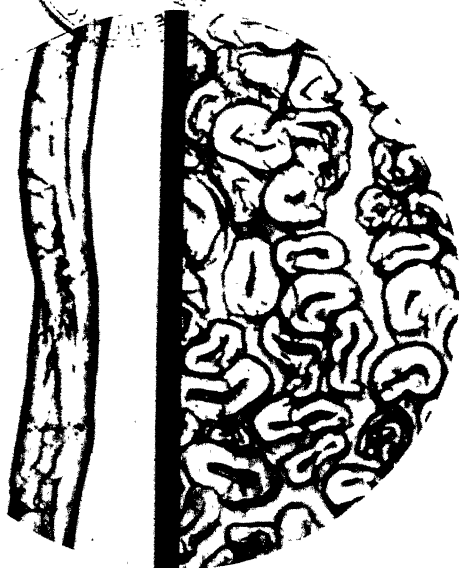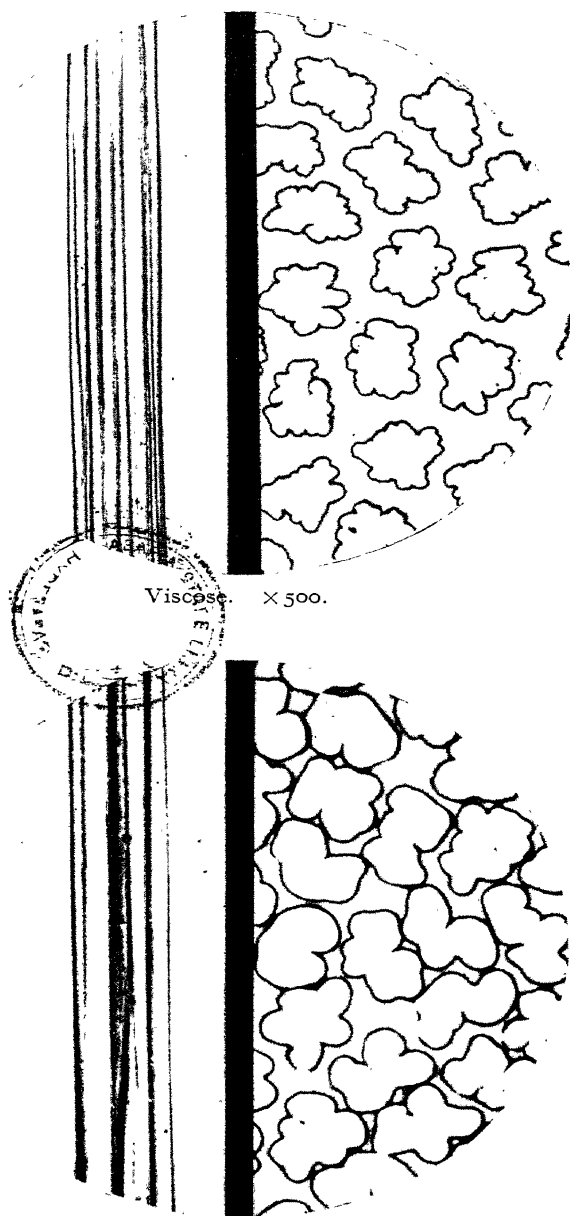
Acetate.   × 500.
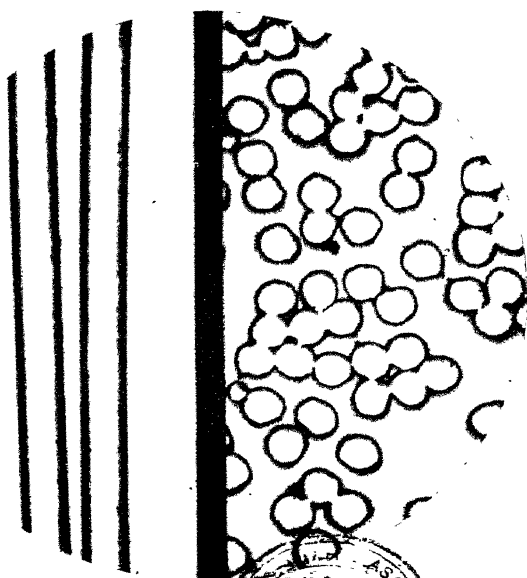
PLATE 3
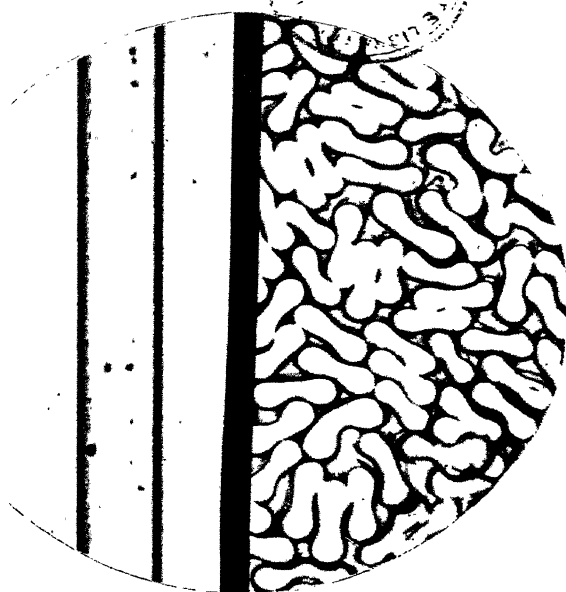
Cuprammonium   × 500.

Vinyon   × 500.

PLATE 4

Jute.   ×250.

PLATE 5
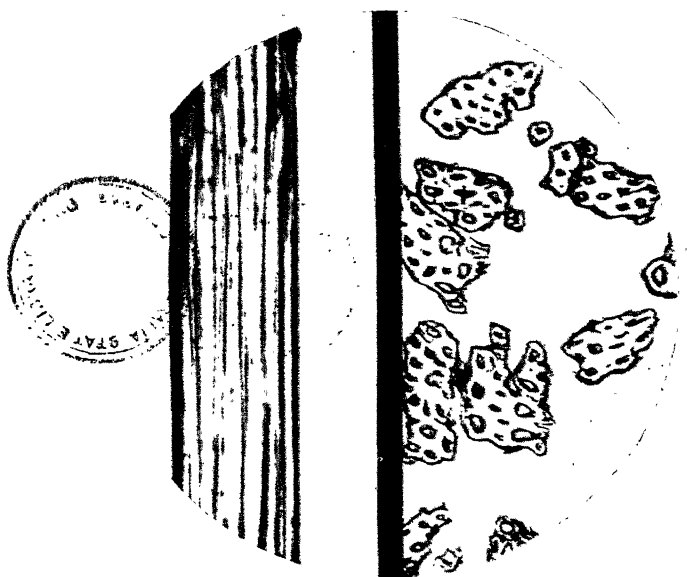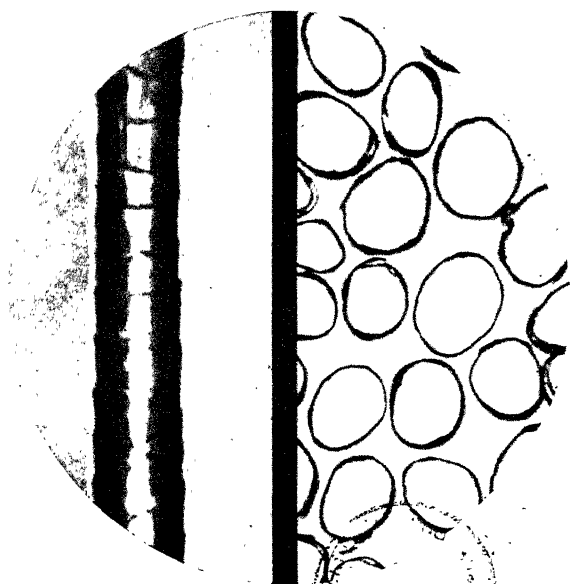
Wool. ×500.

Casein. ×500.

PLATE 6
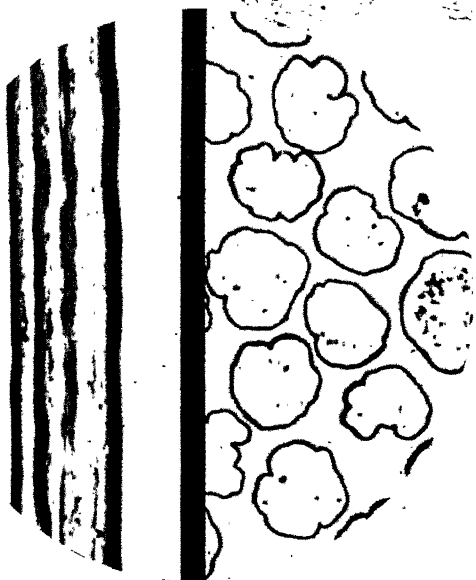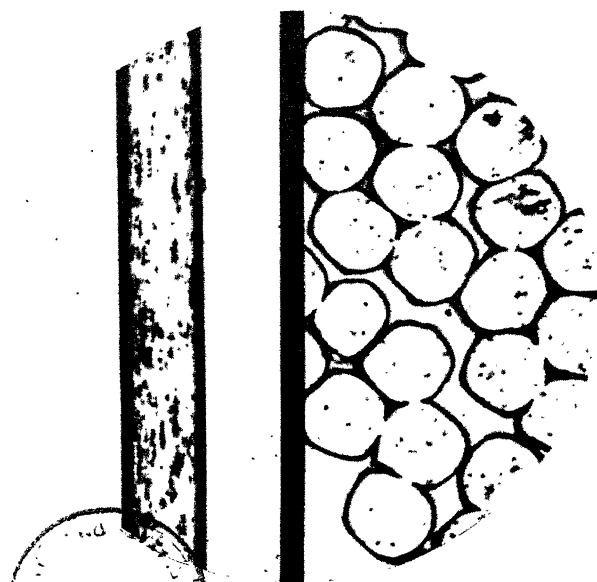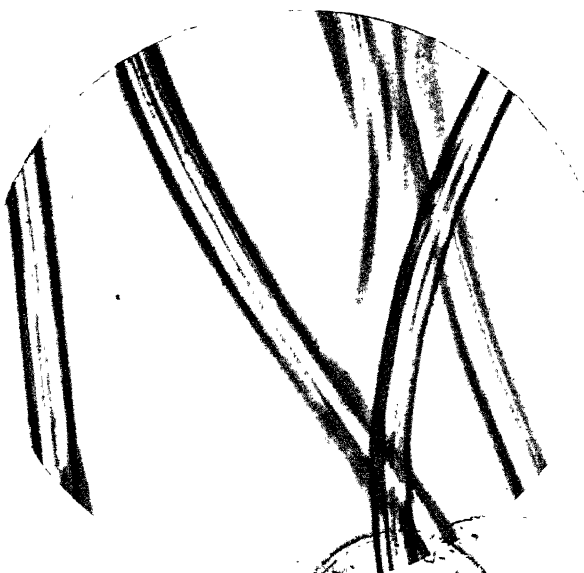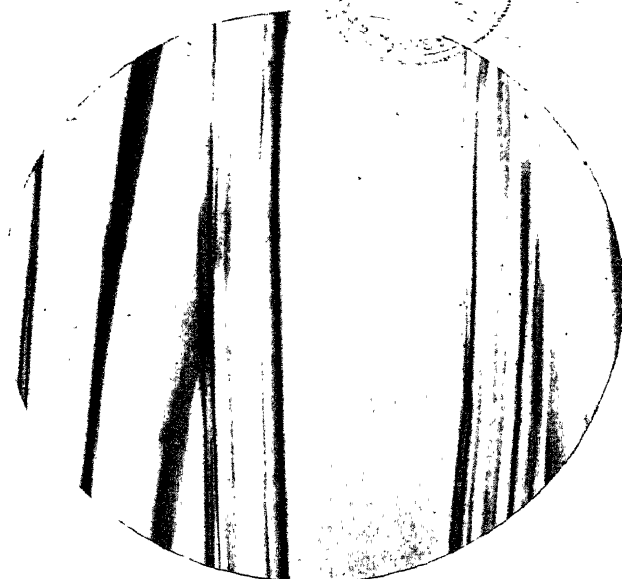

Nylon. ×500.

Natural Silk. ×500
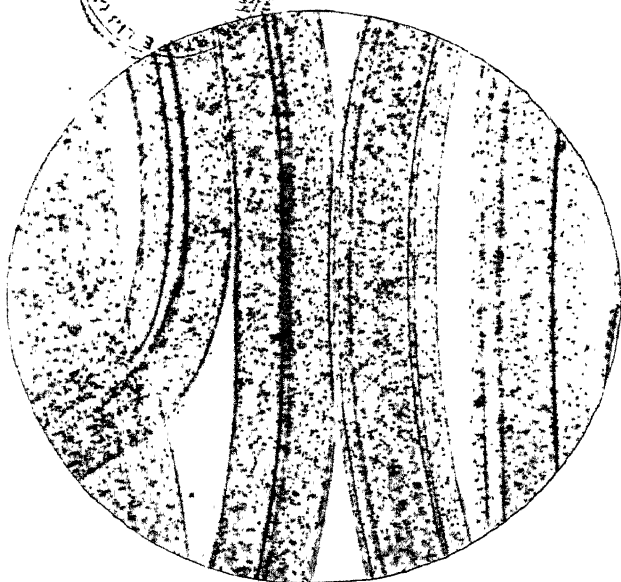
PLATE 7
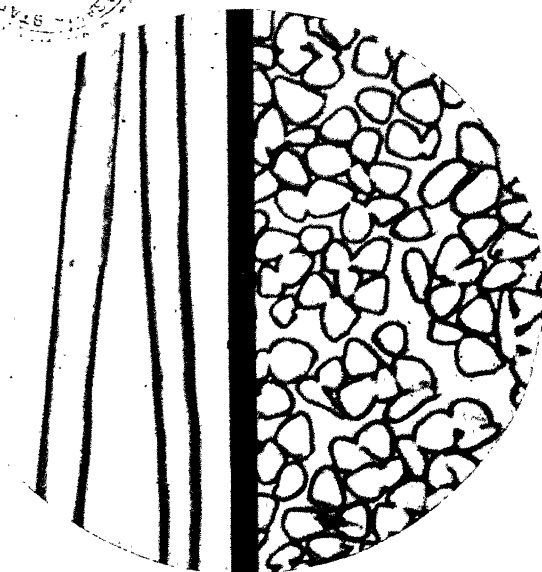
Staple Fibre anti-creased.   Mounted in water.   ×330.

Staple Fibre anti-creased.   Mounted in cuprammonium.   ×330.

PLATE 8

"Rayolanda" X. Mounted in water. ×125.

"Rayolanda" X. Mounted in cuprammonium. ×125.

Microscopical Examination.—The microscopical examination of textile fibres is a rapid and accurate means for the identification of fibres and has the additional advantage of enabling fibres in blended and dyed yarns to be identified, even when only a small sample is available.

In making a microscopical examination a few fibres are placed on a microscope slide, wetted with water, covered with a cover glass and examined, using a low power objective in order to ascertain if a mixture of fibres is present. Examination of individual fibres should then be made using a high power objective. An examination of the cross-section is, in some cases, also desirable, *e.g.* in distinguishing between viscose and cuprammonium rayons.

Microphotographs 1–11 showing the general appearance of a number of fibres under the microscope will be found useful for comparison purposes when making microscopical examinations.

Examination under the microscope does not distinguish between staple fibre (" Fibro ") and " Rayolanda " X. It has been shown (Wilcock and Tattersfield, *J.S.D.C.*, 1941, p. 147) that if the material is mounted on a slide in cuprammonium solution and examined these fibres are easily recognized since the " Fibro " dissolves and " Rayolanda " X simply swells. Anti-creased " Fibro " also swells, but to a much smaller extent (see plates). The cuprammonium solution is prepared by adding 55 g. potassium hydroxide in 50 c.c. water to 1,100 c.c. 0·880 ammonia, then adding, while stirring, 120 g. copper sulphate crystals in 300 cc. water, cooling, and filtering through glass wool.

Section III.—PREPARATION OF MATERIALS FOR DYEING

The object of preparing materials for dyeing is, in most cases, to remove naturally occurring and added impurities (sizing materials) from textiles in order to ensure that they may be dyed satisfactorily. Only a brief account of the various methods employed is given below since, in a book of this size, it is not possible to discuss in detail these processes, which vary widely in different dyehouses.

SILK

Degumming.—It has been stated (p. 27) that raw silk fibres (fibroin) are coated with silk gum (sericin). As the natural lustre and softness so characteristic of pure silk is much less apparent before the gum, which is often yellow coloured, is removed, and as raw silk tends to dye unevenly, degumming is a very important silk preparatory process.

Many interesting methods, including the use of pancreatic extracts and other ferments, have been proposed for degumming silk, but soap solutions are still the most widely used for this purpose. The degumming action of soap solutions is generally admitted to be due to the degradation of sericin by alkali liberated by the hydrolysis of the soap, so that the degumming bath must contain enough soap to produce the necessary quantity of alkali. The use of synthetic non-hydrolysable detergents is, therefore, not recommended for degumming silks, and even the substitution of part of the soap by synthetic detergents is stated to have an unfavourable influence by retarding hydrolysis of the soap (Stockhausen, *Seide*, 1932, p. 387). To produce a sufficiently alkaline liquor an addition of soda ash is sometimes made to the soap bath, and recent work has shown that soap can be completely replaced by the use of Na_2CO_3—$NaHCO_3$ buffer mixtures of appropriate concentration.

40

In practice, raw silk is degummed by treating for 2 hours or more at or near the boil, in a bath containing 25–30 per cent. on the weight of material of a good quality soap. This may be done either by packing the raw silk skeins into bags which are then completely immersed in the soap liquor or by suspending them on sticks and turning so that each end of the skeins is in the liquor for two half-hour periods. Vigorous boiling should be avoided as this tends to entangle the skeins, but the temperature should not be allowed to fall much below the boil as this reduces the efficiency of the degumming. One soap bath is usually sufficient for dark shades, but to produce a whiter yarn for light shades, or when degumming a yellow gum silk, a second treatment for 1 hour in a soap bath containing 15 per cent. soap on the weight of material may be necessary. After degumming, the silk is removed from the bath, drained, hydro-extracted, and straightened out on pegs when it is ready for dyeing. When the degumming is complete the silk has a good scroop. When degumming pieces, care must be taken to avoid using machines which may subject the pieces to friction, or chafe-marks, which persist throughout all subsequent processing, will be caused.

The first degumming bath containing practically the whole of the silk gum is known as " boiled off " liquor, and is subsequently used in dyeing. Several tests have been proposed in order to determine when degumming is complete, one of the most useful being the use of Shirlastain " A " (I.C.I.). The test is carried out by washing the sample quite free from soap, immersing in the cold stain for 1 minute, and again washing in cold water. Raw silk is coloured a very dark brown whilst degummed silk is coloured a slightly brownish-orange. As there is a regular gradation of shade until degumming is complete, the course of technical degumming can be followed, and any deleterious effect of unduly prolonged treatment avoided.

Bleaching.—If silk requires to be bleached this is invariably done after degumming ; the best method being by the use of hydrogen peroxide, with or without the addition of soap or a small amount of ammonia. Thus for 10 lb. silk the bleaching bath is prepared by adding 1 lb. sodium peroxide to 25 gallons of water containing 1 lb. 6 oz. of sulphuric acid, 168° Tw. and then adding ammonia until the liquor reacts slightly alkaline. The

silk is entered at 40° C. the temperature gradually raised to 90° C., and the silk allowed to lie in the liquor for 5–6 hours. The goods are then washed, soured, washed, and soaped.

WOOL

Scouring.—In whatever form wool is dyed it is essential that it be efficiently scoured so that the dyestuff may not be prevented by grease from penetrating the fibre.

Loose wool as it comes into the market contains 30–80 per cent. of impurities which are removed from the fibre by what is known as wool washing. These impurities may be classed as " natural " and " acquired," the first consisting of wool (suint) and fat, which come from the follicles and form a yolk, the second is dirt, sand, seeds, etc., which the sheep has collected, and which are difficult to remove.

It is impossible to lay down hard and fast rules regarding wool washing, as this varies considerably according to the type of wool to be washed : the system of emulsion scouring described below is, however, universal in this country. The washing is usually done by the counter current method, *i.e.* the liquor flows the reverse way to the direction of movement of the wool in a series of long narrow tanks (bowls) in sequence ; 4 or 5 bowls constituting a set. The bowls generally have a depth of 3 ft. and are fitted with a perforated tray about 15 in. deep to prevent the wool from settling to the bottom of the bowl. A number of forks fitted on to parallel bars extending the length of each bowl constantly move the wool forward to heavy delivery rollers which squeeze dirty liquor out of the wool before it is passed to the next bowl. In general, soap and soda ash are used for wool washing, the strength of the liquors used being very varied. A large excess of alkali must be avoided or the wool will be harsh and brittle, thus giving increased fibre breakage in carding with consequent greater waste losses in combing, and the resulting top will have a harsh handle. Faults made in scouring appear in all after-processing, particularly dyeing, so that alkali must be used with care, and the scouring bath must be kept of constant composition by the gradual addition of definite weights of the scouring agents. The following is typical of the constitution of the wash bowls

(quantities required per day) for 4,800 lb. Merino wool of 50 per cent. estimated yield (Wool Year Book, 1941) :

			1st Bowl	*2nd Bowl*	*3rd Bowl*	*4th Bowl*
Length of bowl (ft.)		..	30	30	18	12
Capacity (gallons)	..	..	1,800	1,500	1,000	750
Temperature (F.)	..	..	120	115	110	105
Soap (lb.)	..	..	125	65	40	15
K_2CO_3	..	..	35	5	—	—
Immersion (minutes)		..	3	2·5	2	1·5

After scouring, the wool is well rinsed with soft water.

When loose wool has been opened on the carder and drafted it generally has a poor colour due to added oil and dirt picked up during processing, which is then removed in the sliver by backwashing. In this process the carded slivers are fed from cans to a bowl containing soap, squeezed, and passed to a second bowl, which often contains—besides water—a little soap and blueing agent.

Slubbing is usually dyed " in the oil," *i.e.* the 3–5 per cent. oil from the combing is not washed out before dyeing : in some cases, however, the wool is given a lukewarm wash with soda ash alone or with ammonia and then rinsed.

Most yarns contain oil or grease added to assist spinning and so require scouring before dyeing. If the yarns tend to curl or felt badly they are set before scouring. This is done by stretching the hanks on frames, immersing in boiling water for 30–60 minutes, preferably moving the hanks on the sticks half-way through the treatment, and then cooling whilst still under tension. By this means the yarn is straightened and has then no tendency to curl in subsequent processing. Scouring is done with 2–3 per cent. of soap with or without the addition of 3–4 per cent. soda ash depending upon the yarn to be scoured. It is then well rinsed. With woollen yarns which may contain up to 15–20 per cent. of olein oil, less, or no soap is required, as soap is formed by the action of the soda ash on the oleic acid used in spinning, whereas with worsted yarns, which are oiled with about 3 per cent. olive oil, soap alone is commonly used.

Wool pieces are generally scoured in the dolly, using scouring liquors similar to those used in yarn scouring, but pieces which are liable to crease are best scoured in an open width scouring machine. The dolly consists of a vessel containing strong scouring liquor, similar in shape to that of a large winch (Section IV.), over

which are mounted a pair of heavy wooden rollers.   Underneath
the bottom rollers is a trough which leads the dirty squeezed
liquors out of the machine.   One end of the cloth is run between
the rollers and stitched to the other end, making a continuous rope.
It is then run through the strong scouring liquor for a time, more
water added, and scouring continued until the piece is cleaned ;
the actual length of time depending on the type and quality of
the material being processed.   The cloth is then washed off in
lukewarm water, the water run into the dolly at the same time
as the scouring liquor is being run off.   This is necessary to prevent
deposition of dirty soap on the pieces.   The above method cannot
be used for pieces which are very liable to crease ; these are best
scoured in an open-width scouring machine.   Lightweight fabrics
requiring a clear finish must be scoured for as short a time as
possible.

Many cases of unlevel dyeing prove on examination to be due
to inefficient scouring and inefficient washing out of the soap,
or to the precipitation of lime soaps on the wool due to the presence
of calcium salts in the water or in the wool itself.   These diffi-
culties have led to the introduction of scouring agents, such as
Igepon, Lissapol, and Gardinol (see Section XVII.), which are stable
to hard water and to acids of dyebath strength.   By scouring
in liquors containing the usual amounts of soda ash together
with 1·0–2·0 gms. per litre of Gardinol, Lissapol, Igepon A, or
Sulphonated Ocenol, etc., no precipitation of lime soap occurs ;
moreover the soap, formed from the saponifiable portions of the
wool grease and soda ash used in scouring, is prevented from pre-
cipitating.   As these scouring baths are not exhausted to the
same extent as are soap baths, it is claimed that they remain
usable much longer, whilst the wool is not as liable to felt as
when soap scouring baths are used.   These products are finding
an increasing use in all forms of wool scouring, and have made
possible the scouring of single woollen yarns in the form of cheeses.
When woollen cheeses are scoured with soap it is almost impossible
to wash out all the soap so that when they are dyed in an acid
dyebath the soap is " cracked " and the liberated fatty acids
adhere to the yarn causing uneven dyeing.   As Igepon, Lissapol,
and Gardinol, are not decomposed by acids of dyebath strength
their complete removal is unnecessary, and it was not until the

introduction of these products that wool could be scoured in the cheese form. When soap is used, an addition to the rinsing water of these substances or Calgon removes any lime soap formed on the wool. Lime soap may also be removed from wool by treatment with hydrochloric acid followed by rinsing in a liquor containing dilute ammonia.

Calgon may also be used in all cases where there is a liability to lime-soap formation or for the removal of lime-soaps already present on textiles ; for example, it may be added in loose wool scouring to the last soap bowl.

Pulled or skin wools containing lime may be more cheaply and easily scoured by the use of 2–3 gms. per litre of an auxiliary product, either used alone or in presence of hydrochloric acid than by the usual treatment with hydrochloric acid, neutralizing with soda ash, and finally soap scouring. It is also claimed that this method gives a fibre which is superior as regards strength and cleanliness.

Carbonizing.—This process has for its object the removal of vegetable impurities in wool, and is carried out on loose wool or wool pieces. Rags are also carbonized to remove cotton stitching prior to use in shoddy manufacture. The principle of carbonizing is to convert the cellulose into hydro-cellulose, which crumbles into a powder on rubbing, by a treatment with acids or acid producing salts followed by drying.

Sulphuric acid (6°–8° Tw.) is still the most commonly used carbonizing agent, although aluminium chloride (8°–10° Tw.) or gaseous hydrochloric acid are also used. The goods are immersed in sulphuric acid until thoroughly saturated, hydro-extracted, dried at 60°–70° C. and then heated at 110° C. for a short time. When carbonized the goods are either neutralized immediately or run dry through a dolly or milling machine to remove charred vegetable matter and then neutralized. Aluminium chloride is used to a less extent than sulphuric acid owing to the higher costs of the process, and to the fact that the higher temperatures necessary cause injury to dry wool. Hydrochloric acid gas is used mainly for rags since the colours of the rags do not bleed as much as with a wet process. Carbonizing is a constant source of trouble if care is not exercised in carrying it out. Attention should be paid to uniform saturation of the goods, which should

not be allowed to lie about for any length of time before drying as otherwise the acid will become unevenly distributed and so given uneven carbonizing. For the same reason uneven drying or water spotting, which results in local differences in the concentration of acid must also be avoided. Uneven baking, *e.g.* due to machine stoppage, results in over-carbonized wool which dyes a lighter shade than the rest of the goods (see also Lloyd, " Wool Record," 1932, pp. 1305, 1361). A point which must be particularly watched from the piece dyer's point of view is that wool saturated with acid if exposed to light is so changed that it refuses to take the dyestuff. If, therefore, a piece is so exposed, the dyeing will be very uneven and the piece will be ruined.

For the identification of carbonizing faults, see Hirst (*J.S.D.C.*, 1937, p. 48).

Crabbing.—The object of crabbing is to prevent the curling, shrinking, felting, and creasing of all-worsted and worsted-cotton union fabrics during subsequent dyeing operations. In this process the pieces are passed at full width and under tension through boiling water, beamed and allowed to cool. Alternatively the pieces are run under tension on to a perforated iron cylinder immersed in water, and the water boiled by passing in steam. After steaming, the pieces are allowed to cool and are usually run on to another perforated cylinder and again steamed and cooled. This second steaming is necessary to obtain uniform steaming which, if not obtained, results in unlevel dyeing due to the fact that steaming increases the affinity of wool for dyestuffs. The degree of setting is dependent on the pH of the crabbing water, a low pH producing little setting which is increased to a maximum at pH 9·2 (Speakman, *J.S.D.C.*, 1936, p. 338). In practice, therefore, the pH of the water should be adjusted to the highest pH below 9·2 which is consistent with the necessary fabric strength.

The mechanism of setting has been investigated by Speakman (*ibid.*; Speakman and Stoves, *J.S.D.C.*, 1937, p. 237), who states that the cystine linkages (p. 24) are first hydrolyzed according to the equation :

$$R—S—S—R+H_2O=R—SH—+OH—S—R$$
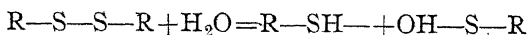
so dissipating internal stresses in the fibre. A permanent set is then given to the relaxed structure by the formation of new

linkages between the peptide chains by condensation of the products of the hydrolysis of the cystine linkage with amino acids, thus :

$$R—S—OH—÷NH_2—R=R—S—NH—R+H_2O$$
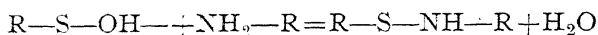
Based on this and subsequent work, Speakman (*J.S.D.C.*, 1936, p. 423) has determined conditions for imparting a permanent set at low temperatures, for details of which the original paper should be consulted.

Milling.—The milling process is based on the property of wet wool fibres to felt when submitted to pressure, especially in presence of soap, alkali, or acid, and has for its object the conversion of fabrics into denser, more durable cloths of more pleasing appearance. As the extent of milling depends upon the type of cloth and the result required, very widely different conditions are employed in milling machines.

Of the three general methods used, soap milling is most widely employed and gives the softer cloths, but the cost is greater than when grease or acid milling is used. There has been much discussion as to the best type of soap to use ; the oleic acid soaps are stated to give maximum softness and a full handle, whereas the stearic acid soaps give firm fabrics. The strength of soap used varies from a 7–10 per cent. solution, the higher the strength the more rapid the milling. Too much soap solution must not be used since if the material becomes too wet the rate of milling is retarded ; about $2\frac{1}{2}$ gallons of a 10 per cent. soap solution should be sufficient for starting a 100 lb. piece. If the pieces become too dry excessive " flocking " may occur, so that further small additions of soap solution should be added. The best working temperature is about 35° C. ; too low a temperature retarding the rate of milling, whilst too high a temperature may give uneven milling.

Grease milling is widely used for lightweight cloths and consists of milling in presence of soda ash solution (about 6° Tw) ; 100 lb. greasy wool requiring about 8–10 gallons of soda ash solution. Any saponifiable oil is converted into soap, so that soap is only added if the pieces become too dry.

Acid milling is extensively used for uniform cloths, felts, and for hat making, the milling agent being sulphuric, formic or acetic

acid ; lactic acid has also been successfully used. It is claimed that acid milling is quicker and gives a greater cloth strength than alkaline milling, but the cloth is somewhat harsher. In this process the best results are obtained by running the scoured pieces in a solution of 2 lb. D.O.V. in 100 gallons of water, hydro-extracting, and running in the milling machine. If the goods run dry, only water is added. After milling the goods are well washed off before dyeing (see also " Wool Record," 1940, pp. 762, 800).

Bleaching.—The yellowish tint of natural wool can, in most cases, be satisfactorily covered by dyeing, so that bleaching is only necessary for white goods and when dyeing pale delicate shades.

Wool is usually bleached in yarn or piece form using either reducing agents (gaseous sulphur dioxide or an aqueous solution of sulphurous acid) or oxidizing agents (hydrogen peroxide, perborates, permanganate, but not hypochlorites). Of these sulphur dioxide and hydrogen peroxide are commonly used.

The operation of bleaching wool with gaseous sulphur dioxide is technically known as " stoving." In this process yarns in hank form are first well scoured (see p. 43) ; tinted with such dyestuffs as Methyl Violet, or Methylene Blue, and hydro-extracted. The hanks are then hung on wooden sticks, taking care that the hanks are not too close together, and placed in closed chambers provided with a suitable ventilating arrangement to enable the sulphur dioxide, produced by burning sulphur to escape after bleaching. Good bleaching is only obtained when the stove is entirely filled with sulphur dioxide ; the average amount of sulphur used is 3–6 lb. for 100 lb. wool, according to the size of the stove. As a rule the hanks are allowed to remain overnight in the stove, air is then drawn through the stove, the yarn removed, rinsed, and dried.

For bleaching pieces the process is the same as for hanks, but the stove is differently constructed, the pieces passing through a slit in the stove, over a number of wooden rollers arranged in two tiers, and out of the stove again at the same slit. The pieces are then washed, and usually blued after stoving.

The change of shade of wool on stoving is not a permanent one, and on soaping the wool again assumes its original yellowish

tint. Again, stoved wool retains sulphurous acid very tenaciously, which may cause trouble by having a bleaching effect on coloured yarns with which it comes into contact. A much improved white is obtained by following the sulphur stoving with a hydrogen peroxide bleach.

Peroxide bleaching of wool may be carried out by using either hydrogen peroxide or sodium peroxide of which the latter is the more generally used. For bleaching 100 lb. wool a bleaching bath is prepared by adding 27 lb. sulphuric acid 96 per cent. to 200 gallons of cold water in a clean wooden vessel, and then slowly sprinkling in 20 lb. sodium peroxide whilst stirring gently. The bath which is slightly acid is made slightly alkaline by the addition of ammonia or sodium silicate, the scoured wool entered, the temperature of the bath raised to 40°–50° C. and the wool allowed to remain in the liquor overnight. Next morning the wool is washed, soured with dilute acetic acid, and finally washed off. This method is more expensive than bleaching by sulphur stoving, but a more permanent white is obtained. In some cases the wool is bleached first with peroxide and subsequently in the stove with sulphur dioxide.

It should be noted that sodium peroxide must be protected from moisture during storage, and must not be brought into contact with wood, paper, etc., or spontaneous combustion may occur. Metallic stains on the material, and iron or copper pipes in the vessel also decompose peroxide which may lead to local tendering of the material.

COTTON

Raw cotton, in addition to moisture, contains about 5 per cent. of impurities consisting mainly of natural waxes, pectic substances, etc., which are insoluble in water, but are removed by hot alkalies. These impurities prevent the easy wetting out of cotton in the dyebath so that, with some exceptions, it is customary to remove the impurities by pressure kier boiling prior to dyeing. In addition to natural impurities the warp threads of cotton cloths contain size used to facilitate weaving which unless removed makes it very difficult to dye solid, well penetrated shades. This is usually accomplished by a desizing process before kier boiling. As cotton, even after kiering, has a

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yellowish appearance it is frequently necessary to remove the natural colouring matter of cotton by bleaching in order to make the dyeing of certain bright shades possible.

Loose cotton is usually dyed in the raw state since removal of the natural cotton wax impairs the spinning properties of the fibre. In order to assist penetration wetting agents may be added to the dyebath, but complete levelness of dyeings is not essential since unlevel dyeings can be evened out in the subsequent carding operation.

Most cotton yarn is wetted out or boiled out before dyeing, whilst if it is to be dyed in light shades it ·is often bleached. Wetting-out is usually sufficient for condenser yarns which have to be dyed in medium or heavy shades, but experience has shown that fine yarns are preferably kier boiled. One method of wetting-out which has proved satisfactory in practice is to place the yarn in bundle form in boiling water, add Lissapol LS to the water (0·95 per cent. Lissapol LS on the weight of yarn being sufficient to enable the yarn to sink) and to allow the yarn to soak overnight. Boiling-out of cotton yarns is essential for the elimination of cotton seeds and is usually done in one of the many forms of low-pressure kiers, the yarn being packed into the kier and boiled with 3–5 per cent. soda ash overnight. When boiling-out at 30 lbs. pressure, the cotton must be entirely covered by the liquor as otherwise the parts of the yarn exposed to the air lose strength and result in unlevelness in dyeing. In order to avoid damaging the goods by trapped air when working under pressure, the kier must not be closed until the kier-liquor is boiling. After boiling-· out the steam is turned off, the pressure carefully released, the kier flooded over the top to remove scum and the liquor let off from the bottom of the kier, simultaneously running in first hot and then cold water from above. This procedure is carried out to avoid kier stains.

For yarn which has subsequently to be bleached (see p. 52) the following kier-boiling process for 2,000 lb. of yarn has been found to give satisfactory results in practice. The yarn is linked, 500 lb. to a chain, packed into the kier, and boiled for 5–6 hours at 30 lb. pressure in a liquor containing 18 gallons 72° Tw. caustic soda, 90 lb. sodium silicate, and 15 lb. soap (castor oil soap being particularly recommended by the Shirley Institute) the volume

of liquor being 900 gallons. The yarn is then washed in the kier as described above.

If necessary, cotton warps are water boiled in a four-box warp machine or they may be plaited into a kier and pressure boiled as described above before dyeing. Cops, cheeses, and beamed warps are either water boiled or boiled out with 3–4 per cent. soda ash, sometimes with the addition of a wetting agent, in the machine used for subsequent dyeing. The actual treatment given in all these cases varies widely, depending upon the shade to be dyed and on the class of dyestuff used.

Cotton piece goods invariably require to be carefully prepared if unlevel results are to be prevented. After being stamped and sewn end to end, linings, sateens, and similar cloths are singed to remove projecting fibres from the surface of the cloth. This is done either by passing the cloth over a heated plate or roller, or by passing the cloth over a series of gas burners, although in present-day practice it is common to combine in one plant gas singeing and plate singeing, and to obtain the desired result in one passage of the cloth. Care should be taken to keep the singe plates or rollers free from scale.

Following the singeing process the goods are then desized. Although the amount of size contained in cloth intended for subsequent dyeing is less than formerly, more importance is now attached to its removal before kier-boiling than was the case a few years ago. The oldest method employed for desizing was to allow the cloth to lie in the wet condition at 35°–45° C. until the starch used in sizing fermented and so became soluble, but this method has been generally replaced by the use of enzymic preparations such as malt extract (Diastafor), pancreatic enzymes (Novo-Fermosol), and bacterial diastases (Rapidase). In using these products about 1 per cent. on the weight of goods is used, dissolved in water and the goods after treatment at 50°–60° C. piled and left overnight. Temperatures exceeding 60° C. should be avoided since at higher temperatures the enzymes are destroyed ; Rapidase, however, can be safely used at 70°–75° C. The activity of these enzymes is also greatly influenced by the pH of the solution, alkali being particularly detrimental, so that neutral liquors should be used. Although controlled acid-steeping and the use of Aktivin (toluene p-sulphonchloramide sodium) are also used

for the removal of size, malt extract probably still finds the greatest use in practice. After the desizing treatment the goods are then washed in warm water to remove the solubilized starch.

The kier boiling of piece goods is carried out in either vertical or horizontal kiers by a similar method to that described above for cotton yarns. For boiling of goods containing coloured yarns, see Section XI. Most of the more recent advances in kier boiling technique have concerned improvements in mechanical design with a view to effecting labour economics. (See Kershaw and Barrett, *J.S.D.C.*, Jubilee issue, 1934, p. 93 ; Scholefield, *ibid.*, p. 108.)

Bleaching.—Goods which require to be bleached or " chemicked " before dyeing are kier boiled as described above, washed in the kier with hot and then cold water, and transferred to stone or slate bleaching tanks or chemicking pits. Bleaching is usually carried out cold with either calcium or sodium hypochlorite solution prepared in a well under the bleaching tank. The liquor is then sprayed on to the goods in the tank, allowed to drain back into the well, a process which is continued until the bleaching is completed. With cotton hanks, treatment for 3 hours with sodium hypochlorite (2 gms. chlorine per litre) followed by washing in cold water, souring with hydrochloric acid ($1\frac{1}{2}$ gallons Tw. to 500 gallons water), and washing with cold water for 1 hour gives a satisfactory white. If the yarn is required for a market white the yarn is then washed with hot water, and tinted in a boiling soap bath with Ultramarine Blue. Research has shown that the pH of the bleaching liquor is an important factor in efficient bleaching (see p. 19). Since this was recognized much of the damage previously associated with bleaching has been avoided.

Although the hypochlorites still find almost universal application for the bleaching of cotton goods, in recent years the employment of other bleaching agents, such as hydrogen peroxide and other per-salts has been advocated. In this connection the opinion has been expressed (Kershaw and Barrett, *J.S.D.C.*, Jubilee issue, 1934, p. 97) " that peroxide bleaching is likely to extend in the future," since it is possible to carry out the boiling and bleaching operations in the same kier. It is, therefore, of interest to note that as a result of work by Du Ponts in America (" Textile World," 1939, p. 63 ; 1941, p. 72) a method of con-

tinuous peroxide bleaching of cotton fabrics has been developed which is capable of bleaching 90–100 yards per minute, the total time required for bleaching being a little over 2 hours, which is only a fraction of the time required for the same goods by the usual kier boiling and hypochlorite bleaching process. Briefly this method consists of saturating the goods with dilute caustic soda solution, squeezing, heating the goods by means of pressure steam and then storing them in a " J " shaped box for one hour at 95°–100° C. washing and squeezing. The goods are then treated for a predetermined length of time in a solution of 0·75 volume hydrogen peroxide and sodium silicate, squeezing, heating, stoving for one hour at 95° C. as described above and finally washing off. Another recent development in bleaching, which is being developed in America by the Mathieson Alkali Co., involves the use of Textone (sodium chlorite, $NaClO_2$) either alone (E.P. 380,488) or in admixture with sodium hypochlorite (E.P. 519,522). When used alone bleaching is carried out in acid solution since it has been shown that there is no danger of oxycellulose formation, and that alkaline solutions have only a mild oxidizing action. Since this process requires radical changes in bleaching methods and, perhaps, the use of special equipment, a mixture of Textone and sodium hypochlorite in alkaline solution has been suggested which may be used without altering the ordinary bleaching procedure (Vincent, Dubean and Symen, *Amer. Dyes. Rep.*, 1941, p. 358). The bleaching solution employed consists of a mixture of sodium hypochlorite and Textone (sodium chlorite) in a ratio of $1\frac{1}{2}$ to 1, in terms of available chlorine and not of equal weight of salts. It is always used at room temperature. The *p*H of the solution is maintained at the desired point—8·7–10, according to duration of the bleaching operation—by using appropriate mixtures of sodium bicarbonate and sodium carbonate. The effect of the addition of Textone, according to Vincent, is to alter the chemical reactions of the hypochlorite. A new product (probably chlorine dioxide) is formed, which is said to bleach without injuring the fibres in any way, thereby making possible the production of bleached cotton goods that are superior in strength to those obtained by the customary method of bleaching. For further details of Textone, see also *Amer. Dyes. Rep.*, 1940, pp. 269, 296, 525; *The Dyer*, Dec., 1940, p. 368). Great care

should be taken when using sodium chlorite, since its use involves both fire and toxicity risks under certain conditions (*Chem. Trade Jour.*, July, 1940, p. 58).

RAYONS

Viscose rayon skeins or cakes usually do not require any preliminary treatment before dyeing since in most cases they are delivered bleached to the dyer, further bleaching only being necessary for the production of certain bright, clear, lingerie shades. In such cases the skeins are treated for 15 minutes in a bleaching bath containing sodium hypochlorite (2 gms. available chlorine per litre), washed, soured, and again well washed.

Viscose rayon warps in fabrics are usually sized with gelatine and starch mixtures which may be readily removed by treatment at 80°–90° C. with a $\frac{1}{4}$ per cent. soap solution. The actual machine used depends upon the type of fabric to be treated. Thus taffetas and satins are desized on jigs, the fabric being kept on rollers all the time to avoid cracks. Fabrics which are not liable to crack in processing may be desized on the winch. Knitted fabrics which are not sized, but simply contain oil used to facilitate knitting are scoured on the winch. In the case of viscose/cotton unions where the cotton warp is sized with starch, the starch has to be removed by means of enzymes on the lines already outlined for desizing cotton pieces (p. 51). Research work on warp stripiness carried out at the Shirley Institute has shown that viscose staple fibre, the bulk of which is warp sized with starch, is capable of absorbing impurities from the malt extract when desized and that the impurities unless removed are dyed darker by some direct cotton dyestuffs. Moreover, it appears to be the regular practice in many quarters to add waxes, etc., to the sizes which will give rise to trouble unless thoroughly removed. It is advisable when wax is present to add solvents, *e.g.* xylol to the scouring bath in order to ensure their complete removal.

The method of preparing acetate rayon piece goods depends upon their construction and constitution, *i.e.* whether they consist of all acetate rayon or are mixtures containing cotton, viscose or pure silk.

All-acetate Rayon Fabrics.—In the preparation of satins, etc., consisting of acetate rayon warp and weft it is essential

that the dyer should receive pieces from the manufacturers as free from cracks, creases, and oil marks as is commercially possible, otherwise it is impossible for him to guarantee that the final finish will be entirely free from these faults, although the trouble can be minimized and in many cases eliminated according to the nature of the creases or cracks by subsequent treatment.

If the pieces are in a bad condition owing to excessive creases or cracks, it is best to wet them out thoroughly on a jigger before scouring : this can be done in a bath containing water only or with the addition of a small percentage of soap at a temperature of 40°–60° C. The pieces can then be hydro-extracted at width in a centrifugal hydro-extractor or run at full width over a vacuum hydro-exhauster, batched, and dried on a hot air-stenter with the minimum amount of weft and warp tension required to take out the creases. As an alternative, they can be run over a belt stretcher blanket finishing machine of the Palmer type provided the steam pressure on the cylinder does not exceed 5 lb. per sq. in. and the pieces are only allowed to remain in contact for just a sufficient length of time for them to dry.

Desizing is a most important operation which contributes very materially to the final results with this type of fabric, particularly as regards " cannage," reppiness, weft barriness, and warp stripiness. The best results are obtained by padding the pieces on the jigger at 60°–80° C. in the following desizing bath—4½ lb. Monopole Soap No. 1, 4 pints caustic soda 45° Tw., 2¾ pints xylol per 10 gallons. The Monopole Soap is dissolved, sieved and bulked, the caustic soda added, and finally the xylol, the whole being thoroughly mixed. This bath can be kept as a standing bath for a considerable length of time. The pieces are allowed to stand for a few hours or overnight after padding, if possible turned occasionally, whilst standing in a horizontal position to prevent too high a concentration of liquor draining to the bottom of the batch. A very good non-slip finish is given by this method of desizing. Other similar methods of desizing give satisfactory, but not quite as good results as the above. The pieces are then scoured with 0·15–0·25 per cent. solution soap (green olive oil) and 0·05–0·1 per cent. solution ammonia (880) at 60°–80° C. for pieces to be bright finished, and at 60°–100° C. for pieces to be dull finished, during ¾–1½ hours.

Pieces to be dull finished are then washed thoroughly and worked in a bath containing 2 per cent. olive oil soap at the boil for $1\frac{1}{2}$–2 hours. If a matt finish is required 0·1–0·25 per cent. phenol should be added to the bath last mentioned, the bath being kept at 100° C. with a closed steam coil for $\frac{1}{2}$–$\frac{3}{4}$ hour. It is necessary to maintain 100° C. and it has been found advisable to use high pressure steam for heating purposes. Green olive oil soap gives better results than other soaps, but it must be a good brand, otherwise dirty streaks may be experienced due to the breaking down of the soap. Care must be taken in dissolving up the phenol which should be added to the bath as a very dilute solution in order to avoid small particles coming into contact with the piece and causing spots. As 100° C. is absolutely necessary for the dullest results it is sometimes impossible to obtain the dullness required on a jigger where this temperature cannot be maintained ; in such cases, the pieces are strung and dulled by the box or book form method. Floating of the pieces is liable to occur at 100° C. and it has consequently been found necessary to fix the heating coils below a false bottom, the connecting pipes being led in and out at the bottom and not down the sides of the vessel. Generally speaking, the best results are obtained by framing the pieces when they have to be dulled at 100° C.

The dullness can be increased by varying the phenol content, and for heavy shades it is necessary to obtain a dullness a little in excess of that required in the finished piece, as there is a tendency for the lustre to increase during dyeing. Dullness also varies with the pH of the liquor and the length of time given ; it must be realized that it is possible to overtreat the pieces and so pass the dullest point, thus obtaining a slightly brighter effect. With regard to the pH of the liquor the best results are obtained at pH 10–11 : at pH values below 10 and above 11 dulling is retarded. This liquor can be used again, but for the second and third baths it is advisable to add 1 lb. of Nekal per 50 gallons and to maintain the phenol content at the strength required, as a loss of phenol takes place during the process. The pieces are finally washed in 0·25 per cent. ammonia solution followed by a thorough rinsing in water.

Acetate Warp and Viscose or Acetate Crêpe Weft Fabrics.—These fabrics are best handled by stringing the pieces

from the selvedge in book form, or framing and then hanging them in scouring boxes sufficiently deep to allow full suspension of the pieces. For acetate warp-viscose crêpe weft fabrics, the box is then filled up with water only or with the addition of 0·1– 0·25 per cent. olive oil soap, and for acetate warp-silk crêpe weft fabrics with 1–2 per cent. olive oil soap. The pieces are wetted out cold and the temperature gradually raised by means of a closed coil fitted under the false bottom of the box, during 1–2 hours for the first mentioned pieces, and 3–4 hours for the last mentioned pieces. These methods usually result in a very satisfactory crêpe, but it is necessary to raise the temperature to that used in any subsequent process or if possible slightly above that temperature, as otherwise there is a tendency for cracking to occur during scouring or dyeing, that is, generally speaking, 80° C. for bright finishes and 100° C. for dull finishes.

With fabrics containing pure silk it is not advisable to give too long a treatment in the degumming process, particularly at 90°–100° C. as saponification of the acetate rayon is liable to take place after 4 hours. If a dull finish is required it would not be possible to obtain the maximum dullness after a prolonged treatment, *e.g.* the maximum dullness of acetate rayon possible by the above process is obtained with 1 per cent. green olive oil soap made alkaline to *p*H 11 at 90° C. for 4 hours.

The above-mentioned process usually results in a fairly satisfactory desizing of the acetate warps. In order to ensure that all the size has been removed it is advisable to treat the pieces in the desizing bath previously mentioned (p. 55). 1–5 per cent. of this is usually sufficient and the pieces can be worked either in the box above mentioned or on a winch for 1–1½ hours at 80° C. for bright finishes, and at 100° C. for dull finishes.

For very delicate tints it may be necessary to give the usual scour previously mentioned for all-acetate piece goods after the above process, but generally speaking, a thorough wash is sufficient. The scouring, if necessary, can be done either in the crêping box or on the winch.

The dull finishing of the acetate warps of these pieces can be carried out as part of the crêping and degumming process above mentioned. For matt finishes the percentage of phenol previously mentioned can be added to this bath, although more level results

are obtained in the two bath process previously mentioned. If, however, standing crêping and degumming baths are kept, it may be more convenient to full finish in a separate bath, which can be done quite satisfactorily on the winch.

With regard to dull finishing and dyeing on the winch the pieces are usually run in the slack rope form. The winch is preferably heated with a closed coil of Monel metal, the vessel being made of wood or any of the various stainless metals, such as Monel metal and Staybrite. Any of the covered cast iron vessels of the Vitrolite or Ebonite type can be used, there being points against and in favour of all of these in works practice. It is essential, however, that the perforated false front should be made of wood, as a metal division is liable to cause patchiness, due to the quick conduction of heat through the division from the stuffing box, which is usually at a higher temperature ; the result would be that as the pieces pile against the division they would be subjected to local variations in temperature, particularly when the whole of the bath is required at the maximum temperature at 80° or 100° C. and, patches duller than the rest of the piece would be formed, especially in the dull finishing process.

Acetate Weft-Viscose Warp Fibres.—These are prepared on the same lines as the 100 per cent. acetate fabrics.

Desizing is usually done on the jigger and as viscose warps generally contain a gelatine size it is necessary to wet the pieces out in cold water only and allow them to stand for some time, preferably overnight. They are then worked in water from 40° to 80° C. during 1–2 hours.

Scouring is carried out on the jigger in a bath containing : 0·1–0·25 per cent. soap and 0·06–0·1 per cent. ammonia (880) at 40°–80° C. during 1–2 hours. The addition to this bath of 1–3 per cent. of the desizing bath previously mentioned will give more satisfactory results.

Cotton and Acetate Fabrics.—Cotton and acetate fabrics are generally treated by the above methods. If, however, it is necessary to bleach the cotton the usual hypochlorite bleach followed by souring with hydrochloric acid and an antichlor is used.

Acetate Warp Knitted Fabrics.—As with woven piece goods it is essential that these piece goods be received from the

knitting machines free from creases and cracks, preferably at width on a cardboard roller, otherwise, as mentioned before, it is impossible to guarantee that the final finish will be free from these faults. If in a very cracked or creased condition, one of the following methods can be tried with a view to minimizing the trouble, as if the pieces are prepared and dyed in this condition, they are liable to " crows feet," due to the cracks or creases dyeing a heavier shade.

(1) Stretch on a fixed pin stenter under reasonable tension and if possible steam lightly.

(2) Wet out thoroughly in water and stretch as above, drying in a current of warm air at $50°-60°$ C. under a minimum tension.

The pieces are generally sewn into the form of a circular knitted fabric, turned inside out and then plaited down. They are then run into the winch in a slack rope form, care being taken to avoid knotting, and scoured with $0·1-0·25$ per cent. soap and $0·06-0·1$ per cent. ammonia 880 with the addition of $1-2$ per cent. of the desizing bath mentioned. Satisfactory results are obtained when the pieces are worked for $1-1\frac{1}{2}$ hours at $40°-80°$ C. for bright finishes and $40°-100°$ C. for dull finishes.

Dull finishing is carried out on the winch, the pieces being run in a bath containing the same percentages of soap and phenol as mentioned before. Particular attention should be paid, however, to the previous remarks regarding dull finishing, and scouring on the winch. With knitted piece goods, another method of winch dyeing giving satisfactory results is that carried out in a bath containing three bellied or concave winches, two of the winches being above the surface of the liquor, one of which is adjustable, and a third below the liquor level. The pieces have a wrapper sewn on to each end, and they are then run over the three winches at width one layer on top of another, the outer wrapper end being sewn on to the inner wrapper end which is run out from underneath to the surface. The piece is wet out in water and the whole is kept tight by the adjustable winch. This last method requires a little practice before giving the best results but it usually results in a finish freer from creases and cracks than the ordinary winch dyeing process, although, of

course, it is not possible to obtain the same production. In some dyehouses, pieces are actually run at full width on a wide winch, this method giving satisfactory results free from creasing if the pieces are constantly attended to and kept at width by the man in charge : the production, however, is small. These pieces in heavy shades are liable to brighten during dyeing and so they must be slightly overdulled in the above process in order to obtain a satisfactory final result.

Acetate Yarns.—Although acetate rayon yarns are usually scoured before dyeing excellent results may be obtained by entering the dry unscoured yarn into the dyebath (see Section XIII.). If scouring is deemed necessary this may be done by working for about 20 minutes at 60° C. in a bath containing 2 lb. soap and 1–2 pints ammonia 880 per 100 gallons.

Section IV.—DYEING MACHINERY

DYEING machinery is designed on two fundamental principles, viz.:

(1) Movement of the material through the dye liquor.
(2) Circulation of the dye liquor through the stationary material, commonly referred to as " pack dyeing."

The first principle is applied on certain machines for slubbing dyeing and to all the rotating roller types of yarn dyeing machines and ball warp chain dyeing machines. Practically all piece goods, except a very limited amount of delicate fabrics, which are wrapped on to a perforated beam and the liquor circulated through the beam, are also dyed in machines of this principle. Pack dyeing is being applied to an ever-increasing extent in machines for dyeing loose material, sliver, roving, cops, cheeses, warps, beams, and skeins. In recent years the second principle has also been applied to the dyeing of viscose rayon in the form of a package known as a " cake " obtained in the Topham box during the manufacture of viscose rayon.

The objects of machine dyeing are to reduce processing and material costs, to increase the rate of production and so reduce labour costs ; also to preserve the quality of delicate materials. Pack dyeing of yarn is particularly advantageous for all knitting yarns because it is necessary for high speed knitting that the yarn should be free from knots and broken filaments. Badly dyed skeins result in trouble in all subsequent processing, whereas pack dyed yarn, owing to its superior condition and freedom from knots, may increase the rate of subsequent processing by 10 per cent. Although, as will be seen later, progress has been made in all these directions, there is still considerable room for improvements in dyeing machinery, which in the authors' opinion can only be achieved by co-operative effort on the part of the trained dyer and the engineer. Two examples will serve to

illustrate this point ; the turbulent dyeing machine (E.P. 441,660) based on the work of Rendell and Thomas (*J.S.D.C.*, 1935, p. 157) and the enclosed jig (E.P. 530,013) which is stated to give more level results in acetate piece goods dyeing.

One of the difficulties which the machine makers encounter is to design small experimental machines capable of reproducing the conditions obtaining in large scale machines. This is particularly so as regards the production of small pumps having the same relative efficiency as the larger pumps, and in the building of small machines capable of being worked with the same liquor to material ratio as the larger machines.

1. Machines Involving Movements of Material through the Dyeliquor

(a) **Hand Dyeing.**—There are many yarn dyers and some slubbing dyers who still use the old method of hand dyeing. Although this cannot strictly be termed machine dyeing, since the material is moved by hand through the dyeliquor, this is considered to be a suitable place to discuss this method of dyeing.

In hand dyeing, the hanks are hung on to smooth hardwood sticks or metal tubes, which are then laid across an open rectangular dyebox (or beck) with a false bottom and of sufficient depth so that the yarn is clear of the false bottom of the dyebox. Yarn sticks made from steel tubes covered with hard rubber, or from Monel metal or stainless steel without a rubber covering will be found most suitable for dyeing rayon yarns, since their smooth surface does not fret the rayon, whilst they are also easily cleaned when changing from one shade to another. Bamboo canes are also largely used, though these are very liable to split on hard usage. Lots of up to 100 lb. of yarn are usually dyed, two workmen being required to carry out each dyeing, one standing on each side of the dyebox. The yarn is entered, turned by hand at one end of the box, and pushed stick by stick (travelled) to the other end where it is again turned. This is repeated until the lot has been dyed to shade.

When dyeing rayon yarns by hand there is a great danger of ended skeins, owing to the strong affinity of the rayon for many dyestuffs, unless the skeins are turned quickly at the outset, so that four men instead of two should be employed for a lot of

100 lb. Discretion must also be exercised in the rapid turning and travelling of the yarn or trouble will be experienced in the subsequent winding.

To prevent dilution of the dyeliquor by condensation of steam it is preferable that the liquor should be heated by a coil. As heating a dyebox by a steam coil is slow, an open steampipe should also be fitted, so that the dyeliquor may be boiled by direct steam and then kept at the boil by means of the coil.

The high labour costs, the variables introduced by the human element and the general inefficiency of hand dyeing is resulting in the substitution of this method of dyeing by mechanical dyeing, so that it is rapidly losing much of its former importance.

(b) **Klauder-Weldon Type of Machine.**—This type of
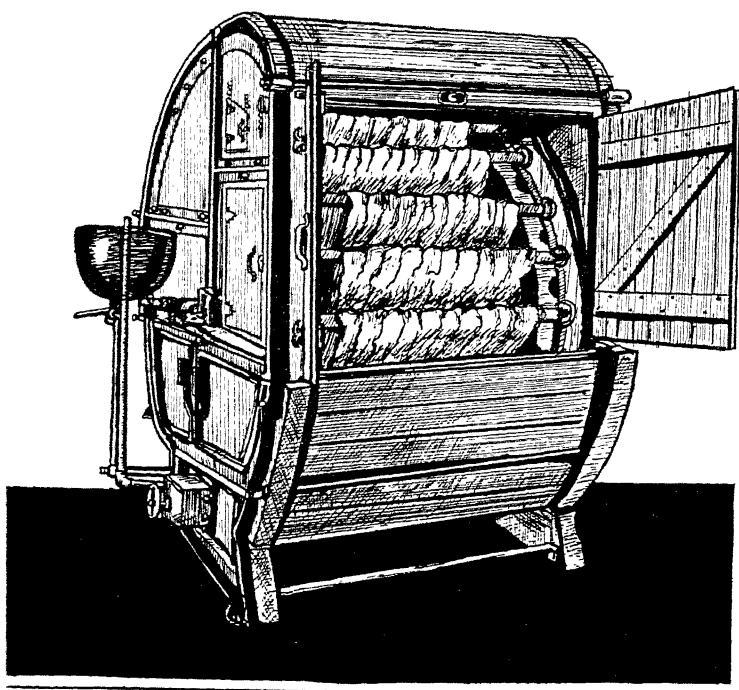
FIG. 1.—Klauder-Weldon machine.

machine is largely used for the dyeing of slubbing in hank form and cotton and wool hank yarns. Briefly, it consists of a large wheel with radial spokes enclosed in wooden case (see Fig. 1).

The hanks are hung on poles, two poles for each set of skeins, which are placed on the spokes so that they are spaced radially from the centre to the circumference of the rotating wheel. At each slow revolution of the wheel the hanks are submerged half the revolution and are above the dyeliquor during the other half of the revolution, whilst to prevent stick marks, the poles are automatically given a partial turn with each revolution of the wheel. At the end of the operation the entire wheel in some types may, if desired, be lifted clear of the dyeliquor for unloading purposes.

This machine is rather cumbersome to handle, but has the advantages that very little steam gets into the dyehouse, so saving steam due to being enclosed, and that the material remains hot when not in the dyeliquor. It is, however, unsuitable for dyeing cotton yarns with vat and sulphur dyestuffs, owing to the great exposure to the air which takes place during dyeing. In slubbing dyeing a lofty open sliver is obtained, but if the dyeing is too prolonged the sliver becomes felted and broken ends may wrap round the poles, thus causing considerable waste. According to Isles (*J.S.D.C.*, 1937, p. 420) slubbing dyed on this machine retains the elasticity of the fibre in a very high degree and many spinners still prefer this method for dyeing fine merino wool. This machine has been used for rayon dyeing in the United States and Canada and, to a smaller extent, in Great Britain, but the authors consider it unsuitable owing to the drag on the yarn when the poles are turned.

(*c*) **The Rotating Roller Machine.**—This type of machine, originally designed for the dyeing of natural silk, is now widely used for the dyeing of cotton and rayon hanks ; it is unsuitable for wool hank dyeing since the wool felts badly and the dyebath cannot be kept at the boil. Working at the actual boil is impossible owing to entanglement of the hanks.

The machine (Fig. 2) is fitted with porcelain, Pyrex glass, monel metal or stainless steel rollers rotated by a crank motion which balloons the yarn in a similar manner to that which takes place in hand dyeing when the yarn is travelled. A recent development in this type of machine is the employment of smaller square rollers rotated by a straight shaft motion, instead of the normal crank motion, which gives an improvement in the con-

dition of rayon yarn in particular. The driving mechanism is so arranged that the rollers automatically reverse each minute whilst the hanks themselves make a complete rotation twice each minute. The rollers have a capacity of 3–4 lb. per roller, and can be arranged in sections of any desired number of rollers from 1 to 20, each section being independently raised or lowered by hydraulic power. The sections may be repeated, the largest machine made having four sections of 20 rollers each. In some machines a large dyebox divided into smaller boxes by means of removable partitions is employed so that the sections of the machine can be used separately or together. Since by constant use the partitions become badly fitting the authors deprecate their use owing to the danger of leakage of dyeliquor from one box to
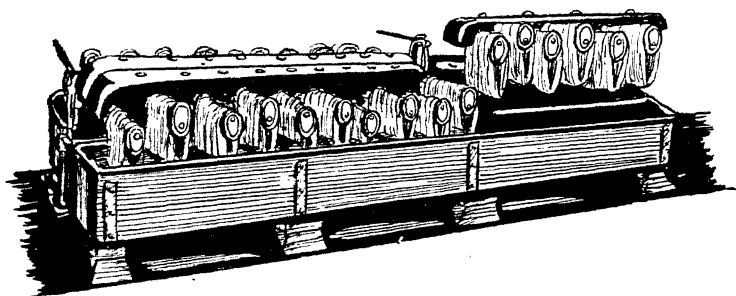
Fig. 2.—Hank-dyeing machine.

the next. Formerly this type of machine was only made abroad by Gerber, Llump and Mayoux, but is now made in this country by Sellars. Its great advantage over hand work is that the whole of one batch of yarn, whether 1 lb. or 400 lb., may be entered or removed from the dyeliquor simultaneously, whilst the whole of the hanks are completely turned in half-a-minute—this is obviously impossible of achievement by hand. The disadvantage of the machine is that the yarn does not spread on the roller, but tends to ball together at low temperatures, a fault which may be overcome by hand turning on the roller. The yarn spreads most easily in a hot dyeliquor containing soap or sodium sulphide. In cases of large weights of yarn any addition of shading dyestuffs must be uniformly and intelligently added to the long narrow dyebeck.

The Smith-Drum [U.S.A.] hank dyeing machine, which is

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similar in principle to the roller dyeing machine described above, utilizes a hollow, perforated, cylindrical arm placed at such a height that the yarn hung on the arm does not touch the dye-liquor in the box below. For the best results the hanks should be placed in a single layer on the arm. The dyeliquor is circulated by a pump, sprayed through the yarn from the perforations, flows down the hanks, and returns to the dyebath below. At controllable intervals the arm rotates and turns the hanks about one-third, so altering their position and avoiding channelling. It will be seen that this construction provides almost the features of a package machine ; large flow of liquor and only little move-ment of the hanks. Such a machine is necessarily more expensive than the roller type, but in the authors' opinion no better results are obtained on it than can be obtained by a well-trained operative on the normal type. As the dyeliquor is exposed to the air more than in any other machine, it is not well-suited for vat dyeing owing to the rapid oxidation of the leuco vat dyestuffs.

(*d*) **The Chain Warp Dyeing Machine.**—This machine is widely used in Britain and the U.S.A. for the dyeing of cotton warps, but finds little use on the Continent. The principle of the machine is illustrated in Fig. 3, which shows a single-box warp-dyeing machine.
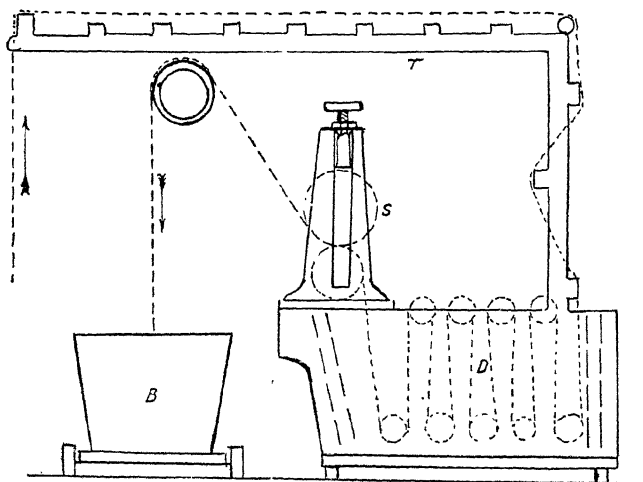
FIG. 3.—Single-box Warp-dyeing machine.

Warp-dyeing machines with several compartments, which are simply repeats of the single-box machine, are more commonly used than the single-box machine. The warps are guided through the dyebath by immersed guide rollers arranged so that the warps pass up and down through the liquor. They are then squeezed through rubber covered squeeze rollers to aid penetration and levelness and pass into a truck. This process is termed giving the warps " one end." Light and medium shades may be dyed in a single passage, but dark shades require several passages in order to obtain the desired shade. The uniformity of shade from end to end of a dyed warp varies with the difficulty of the dyeing process, and largely depends upon the skill and judgment of the foreman dyer when feeding in the previously dissolved dyestuffs. Continuous feeding in of dyestuff from a drip can is used by many dyers to prevent ending of the warps. The authors do not favour this type of machine for " Fibro " warps, but advise they should be dyed by the " pack " system.

Dye Jiggers.—The jig or jigger is a machine designed for dyeing piece goods at full width. In its simplest form it
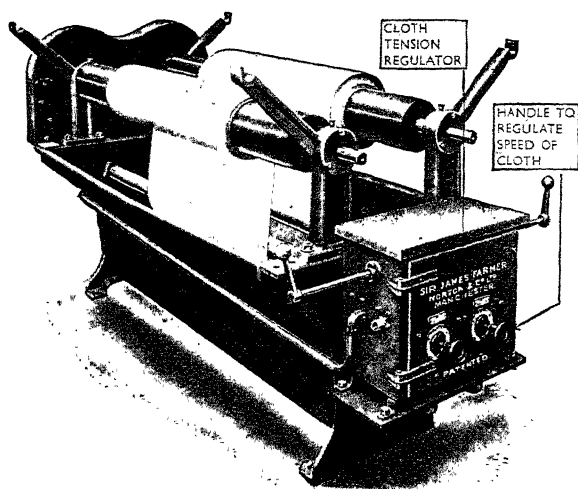
Fig. 4.—Modern jigger (Sir J. Farmer & Co.).

consists of two 6-in. diameter wooden rollers fixed above the sides of a wooden dyevat equipped with immersion guide rollers. The goods are wound on to one of the rollers, passed through the

dyeliquor, and rewound on to the other roller. A leather strap, fixed at one end with a weight at the free end, runs over a pulley attached to the roller and acts as a brake, thus maintaining the pieces under tension. By suitable gearing, the cloth may be run to and from either roller as desired ; in practice an even number of ends (passages through the liquor) is always given to avoid dyeing one end of the cloth to a darker shade than the other end. At no stage of the dyeing should the pieces on the roller be allowed to remain in one position for any length of time, as the dyeliquor retained by the cloth will drain to the bottom, and the lower layers of cloth will tend to be dyed darker than the upper layers, thus resulting in unevenness. Again, when dyeing vat or sulphur dyestuffs the cloth should be evenly wound on to the roller with coincident selvedges, since overlapping selvedges will be rapidly oxidized and during further passages will take up more dyestuff than the bulk of the cloth, thus giving dark selvedges which is one of the undesirable features of jigger dyeing. The main defects of jiggers of this type are—that the wood absorbs dyestuffs and chemicals, and tends to carry traces of them from one operation to the next ; that the cloth travels through the dyebath too slowly at the start and too rapidly at the end of the passage, and that the tension of the cloth cannot be accurately controlled, a feature which is particularly detrimental when dyeing cloths having a synthetic fibre warp.

The most modern jiggers (Fig. 4) are constructed of stainless steel, and have lightweight rollers running on ball or roller bearings. Both the take-up and let-off beam rollers are simultaneously driven through differential mechanical or electrical mechanism with the speed of each beam adjustable, so that tension on the cloth can be accurately varied and controlled. A differential driving mechanism changes speed so that the cloth passes through the dyebath at a uniform rate regardless of the varying diameter of the roll of cloth. The jig may be set to reverse automatically the direction of operation a given number of times and to stop after a predetermined number of passages. It can be set to oscillate automatically the cloth at the end of a passage, *e.g.* whilst patterning, so that the dyeliquor is prevented from draining to the bottom of the roll. Expanders may also be fitted to keep the fabric uncreased and at full width so that it dyes more uniformly.

Various modifications of the jigger have been designed for special purposes, *e.g.* the total immersion jigger which is particularly designed for the dyeing of sulphur and vat dyestuffs, since oxidation during dyeing is prevented. With this machine observation of the cloth is difficult, so that there is always the possibility of it being damaged during dyeing. In jigger dyeing most of the actual dyeing does not take place whilst the cloth is running through the liquor but when it is on the roller prior to going through the dyeliquor again. Since the temperature of the roll is usually about 60°–70° C., although the dyeliquor is at the boil, dyestuffs which give maximum colour value at 60°–70° C., are best for jigger dyeing.

Padding Mangles.—The padding mangle or foulard consists
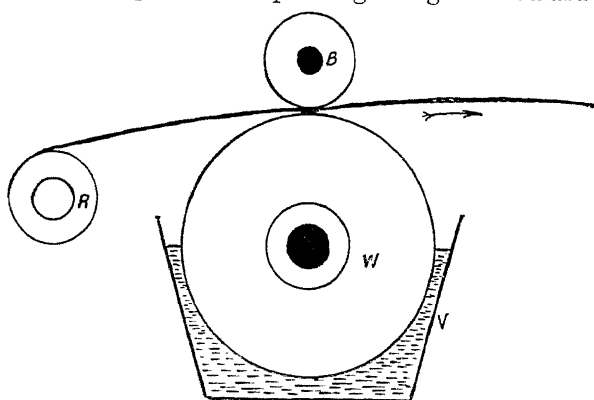
Fig. 5.—Slop-padding machine.

essentially of two squeezing bowls (rollers), the upper one of iron covered with rubber, the lower one of brass or vulcanite, arranged over a shallow trough fitted with two or three freely rotating guide rollers. Pressure on the bowls is obtained by an arrangement of compound levers and weights. The cloth enters the trough through tension rails, passes through the dyeliquor, is uniformly squeezed between the bowls, and then is either batched or passes directly to some subsequent operation. Various modifications of the two-bowl mangle described above are also used : in one form (Fig. 5) the bottom roller runs in the dyeliquor contained in the trough. This latter type, known as the slop-padding machine, is suitable for light-weight goods which are simply run through the nips, the lower roller transferring sufficient

dyeliquor from the trough to saturate the material. This type of machine is unsuitable for heavier goods, which must pass through the dyeliquor, or the dyestuff will all be on one side of the goods.

Three-bowl mangles having a rubber covered middle roller and two brass or vulcanite rollers are also widely used (Fig. 6), whilst other machines with four or more bowls have been designed, but do not appear to have been adopted to any extent. In the case of the three-bowl mangle it is necessary to gear the two
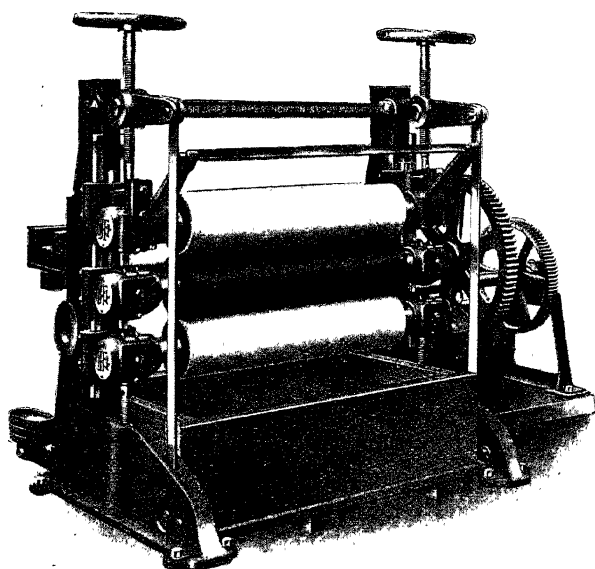
FIG. 6.—Three-bowl mangle (Sir J. Farmer Norton & Co.).

vulcanite bowls together to prevent slip between the rollers, and to prolong the life of the rubber covering. The advantage of the three-bowl mangle is that it allows an immersion in the dyeliquor, and a double squeeze, thus giving better penetration of the cloth, particularly when dyeing azoic and vat dyestuffs.

The results obtained by padding light to medium shades on mangles are excellent and cheaper than those produced on jiggers : speeds of up to 200 yds. a minute being practicable. By combining a three-bowl padding mangle with a series of roller

vats, squeeze rollers, skying rollers, and drying devices a continuous range may be created to give a high production rate and good uniformity of shade over a large yardage. Excellent results are also obtained by the pigment padding vat process (Section XI.) by padding on a three-bowl mangle, followed by subsequent reduction and development of the dyestuff on the jigger.

Winch Machines.—This machine, one of the earliest forms of piece dyeing machinery, consists of a driven winch extending the full width of a dye vat having a perforated partition at the front for steam pipes and for adding dyestuff solution. The actual design of winch dyeing machines varies considerably, some having rectangular or V-shaped dyevats, whilst in others the dyevats are, in section, the shape of a quadrant of a circle. Again some machines are provided with a means of reversing the direction of the winch which may be circular or elliptical in shape, whilst in other machines the winch may not be so reversed. Machines for dyeing at open width have a guide bar or roller fitted in front of the winch, whilst when dyeing in rope form it is usual to provide a peg rail instead of a guide roller so that the drafts may be kept separate and prevented from tangling. In some machines a device is added to the peg rail so that if entanglement does occur the drive of the winch is automatically cut off and damage to the fabric prevented. The older type winch machines were constructed of wood or iron with wooden winches, but in the more modern types the dyevats are lined with monel metal, stainless steel or vulcanite, and are fitted with stainless steel winches. These changes allow of easier cleaning of the machines and reduce friction to a minimum. If machines are used which are of wooden construction (unlined) it is very important that no cracks or fissures are present, otherwise the fabric may be chafed : a modern winch is shown in Fig. 7.

In using these machines one end of the fabric is passed over the guide or peg rail and over the winch. The fabric is then run into the machine and the two ends sewn together so as to form a draft or band of fabric, which is continuously drawn out of and into the dyebath by the action of the rotating winch. During the operation of dyeing the fabric piles down in the liquor at the back of the dyevat until it is drawn out again by the winch. In the large machines several drafts are dyed together.

Wool, worsted, soft cotton, silk, and rayon fabrics which are not likely to crack or crease may all be dyed on winch machines. The machines used for silk and rayon, however, differ from those used for wool and cotton in that the dyevat is shallower and a long rectangle in section ; such machines are also sometimes fitted with a small ball-bearing mounted rubber winch instead of a peg rail over which the fabric runs   An elliptical winch is also
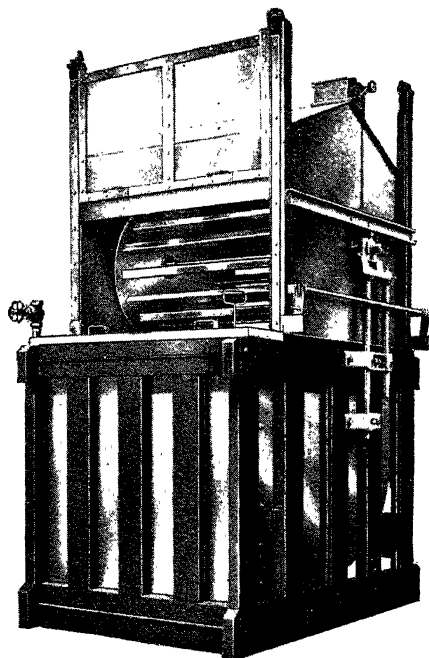

Fig. 7.—Enclosed winch dyeing machine (Samuel Pegg and Son).

fitted which plaits the fabric in folds as it falls into the dye-liquor, and keeps it more open than does a circular winch, so reducing any tendency to unevenness.   In the case of a machine with the drive direct to the elliptical winch the cloth speed is variable and friction marks may be created.   According to Mace (*J.S.D.C.*, 1936, p. 422) one form of machine has been designed to give constant speed of the cloth as it passes through the liquor and over the winches, whilst all snatch or jerkiness between the winches, which give rise to friction marks, bruises, and other defects, is avoided.

A development of recent years is the totally enclosed winch machine which economizes steam consumption by reducing radiation losses, reduces the amount of steam in the dyehouse, and enables more uniform and better penetration to be obtained with certain classes of goods (see Fig. 7).

The Star Frame.—This machine, also known as the Etoile

ADJUSTING SCREW
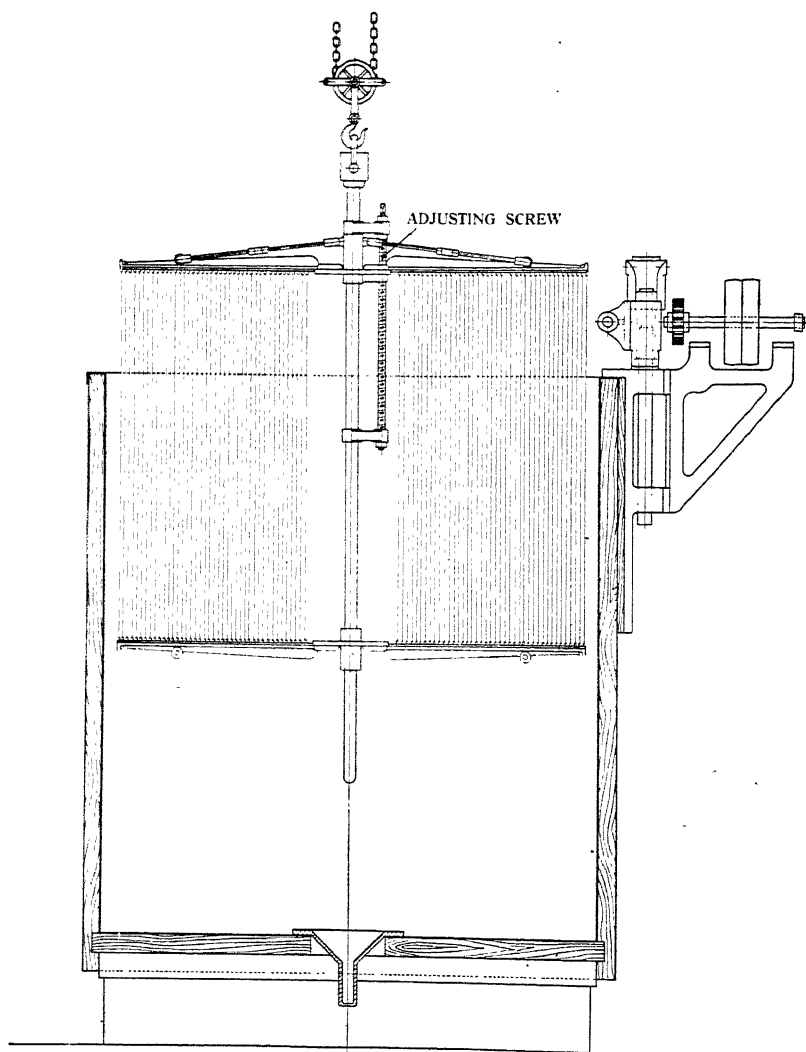
FIG. 8.—Star Frame dyeing (Mather and Platt, Ltd.),

dyeing machine, is particularly suitable for dyeing delicate fabrics, such as crêpes. Cloth varying in width from 32/52 in. may be dyed in this machine in lengths of up to 340 yds. at one time, the cloth being wound spirally on to a portable reel consisting of two star frames fitted to a central shaft (Fig. 8). The hooks for supporting the cloth are attached to each frame by a special method so that they do not become loose, whilst the machine is so arranged that tension can be applied to the cloth and also adjusted during the dyeing operation. When the reel is lowered into the dyevat and completely submerged in the dyeliquor a combined rotating and vertical reciprocating motion is given. This gentle, but very efficient motion results in even dyeing of the cloth without damage. to it. The output of the machine may be increased by charging a second reel with cloth whilst the first reel is being dyed.

2. Machines involving Movement of Dyeliquor through the Material (Pack Dyeing)

The Obermaier Type Machine.—This type of machine consists of a circular perforated container with a solid bottom shown in Fig. 9, which when packed with the material to be dyed fits on to a seating at the bottom of a circular dyevat connected by piping to a centrifugal pump. A solid lid fits on to the container and through it passes a spindle with threads cut at the lower end. These threads (1) allow the lid to be screwed down so that it just touches the material, (2) fasten the lid to the container, so that the latter can be removed from the dyevat by means of an overhead crane, and (3) lock the container to the bottom of the dyevat. The complete unit, which in modern machines is constructed of stainless steel, is shown in Fig. 9. In using this machine sufficient dyeliquor is prepared to immerse completely the container, the container screwed down, the pump started up, and the dyeliquor circulated. With the older type of machine the dyed material had to be removed from the container for hydro-extraction, but with the more modern machines provision is made for hydro-extraction in the container. It is sometimes desirable to retain dyeliquors for further use ; in such cases reserve tanks may be connected to the machine for the storage of such liquors.

The Obermaier type of machine is largely used, particularly on the Continent, for the dyeing of loose wool, cotton and staple fibre, the material being packed fairly tightly and evenly to prevent movement during dyeing. By the use of these machines, the material is less matted and so gives a lower carding and combing waste than is given by simply throwing the fibres into an open dyevat and hand poling, a method which is, however, still largely used. There is also a saving in labour, whilst the resultant dyeing is more even. In addition to loose material, these machines are also suitable for the dyeing of slubbing in
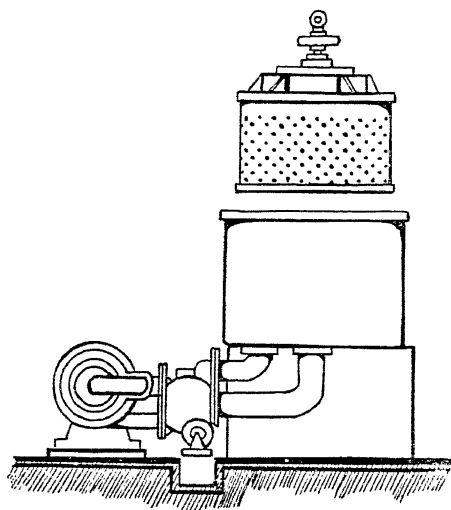
FIG. 9 —Pack dyeing machine.

hank form, and for cotton and staple fibre in both hank and warp form. Hanks are laid evenly and firmly in the machine, each layer of hanks being placed so that they cover the interstices between hanks in the preceding layer : warps are plaited down into the machine so as to form a uniform package.

Cylinder or Can Dyeing Machine.—This machine (Fig. 10) is designed for the dyeing of sliver or tops, whether of worsted or staple fibre in ball form and in hank form. It consists of a series of cylinders or cans having perforated lids into which the tops are placed. The cans fit in to a frame in the dyebath, which is connected to a pump. According to the type of machine the

circulation of the liquor may be either one or two-way, whilst with some machines individual cans may be disconnected from the
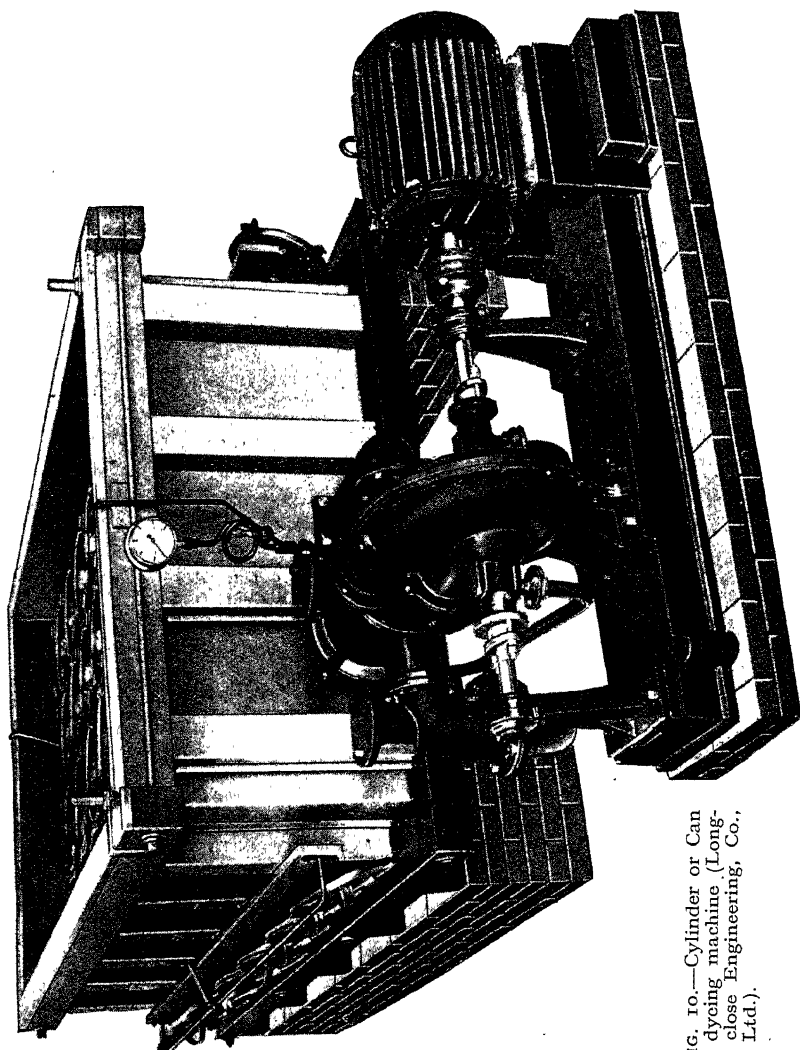
Fig. 10.—Cylinder or Can dyeing machine. (Longclose Engineering, Co., Ltd.).

liquor circulatory system so enabling smaller weights to be dyed in the same machine.

Isles (*J.S.D.C.*, 1937, p. 420) states that with wool " the sliver

from this type of machine has a much flatter or tapey appearance "
(than when dyed on the Klauder-Weldon machine) " owing to
the pressure of the liquor through the material.   If the pressure
is too high the elasticity of the fibre is impaired.   When the
machine is packed with tops of a suitable size, level dyeing is
good.   Shading dyes, however, are liable to give very uneven
results and, in consequence, it is advisable to divide a lot into
two or three dyeings to avoid shading.   Prolonged dyeing does
not felt the sliver and there is no waste.   For the shorter qualities
of wool, such as those used in the French worsted system, this is
the only satisfactory method of dyeing as the sliver is not strong
enough to dye in the Klauder-Weldon or Hussong type of
machine without producing many broken slivers and consequent
waste."

Cop Dyeing Machines.—Yarn in cop form is usually dyed in
a machine consisting of a holder in the form of a hollow cylinder
or frame to which are attached a number of hollow perforated
spindles upon which the cops are fitted.   When the cops are in
position the loaded holder is placed into a suitable vessel, and
the dyeliquor run in from an expansion tank.   The dyeliquor
is then circulated by means of a pump through the perforated
spindles and the yarn, so that each cop receives individual
treatment.   In order to ensure uniformity of dyeing the direction
of motion of the dyeliquor is altered from time to time by
reversing the pump.   After dyeing, the cops are removed from
the spindles and hydro-extracted.   Prior to dyeing cotton cops
may either be boiled out' in the dyevessel using a suitable
wetting agent, or they may be kier boiled, depending upon local
circumstances.

Machines of this type differ chiefly as regards the shape of the
holder, and the method by which the spindles are fixed.   In
some machines the spindles are rigidly fixed to the holder, whereas
in others, the spindles are loose and require to be screwed or
plugged into the holder.

Dyeing in cop form eliminates the necessity of winding spinner's
cops into hanks, dyeing and rewinding into cop form again for
use as weft in weaving.   The dyed yarn is also left in better con-
dition, *e.g.* there are less knots, since entanglement of threads
during unwinding and rewinding is avoided.   On the Continent

cop dyeing has been widely practised, but in this country it has not been developed to the same degree.

Cheese-Dyeing Machines.—There are various designs of machines in use for cheese-dyeing, differing mainly in the mechanical devices used for packing the cheeses and in having either open
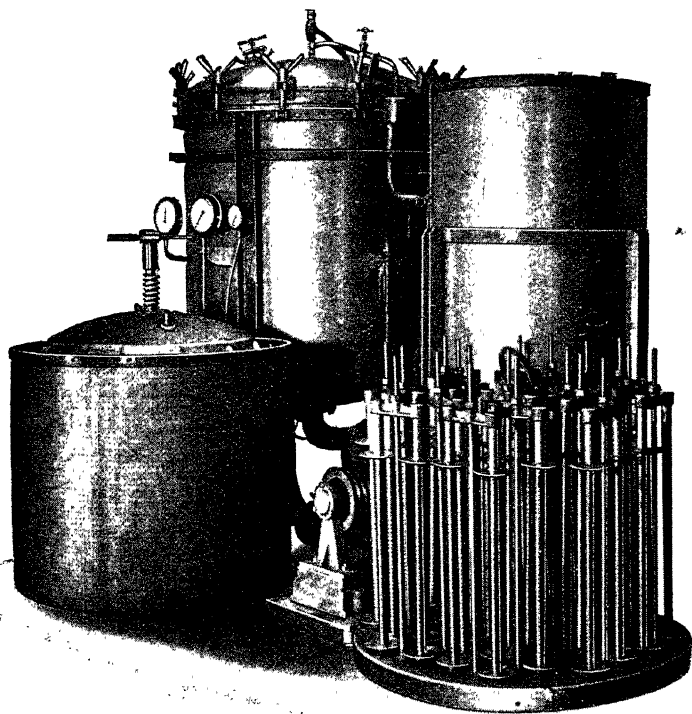

Fig. 11.—Cheese dyeing machine (Longclose Engineering, Co., Ltd.).

or closed (on the autoclave principle) dyevessels. (See Jowett, *J.S.D.C.*, 1939, p. 251).

In one type of machine the yarn is wound on to smooth wooden bobbins having a diameter slightly larger than that of the hollow perforated spindles upon which they are dyed. The spindles are loaded by placing the end of the bobbin on the top of the spindle and pushing the cheese off the bobbin on to the spindle ; each spindle holds up to six cheeses. When the cheeses are in position a pressure head is then screwed down to pack the cheeses together

and to ensure that no leakage occurs between the cheeses when the dyeliquor is pumped into the spindles and through the cheeses. The spindles are then placed into a frame or carrier which may be entered or removed from the dyevessel by means of an overhead crane as required. Depending upon the make of the machine the dyeliquor is circulated by means of a propeller or a rotary pump.

In a second type of machine, cheeses wound on to perforated tubes of such a length that the tube projects $\frac{1}{2}$ in. at each end of the cheese are used. These cheeses are packed in a dyevessel with a false bottom, having suitably spaced holes of a size large enough to allow the end of the tube to be inserted. A cheese is placed vertically on the false bottom, the lower end of the tube in a hole, and upon it is placed a porcelain disc about 2 in. thick, having a hole through the centre. In all, three cheeses are placed vertically end on end, being separated by discs, and on top of the column a heavy porcelain disc is placed to compress the cheeses and prevent channelling of the dyeliquor.

Cheese dyeing is not one of the simplest of dyeing operations and much of the success depends upon the careful winding of the cheeses. If the cheeses are too slackly wound they collapse on handling ; if too tightly wound penetration difficulties are experienced. Moreover, if some cheeses are more tightly wound than others, then the dyeliquor will channel through the slack cheeses. This unevenness of winding tension is largely compensated by pressing the cheeses together, since the soft wound cheeses compress more easily than the hard ones. Another difficulty in cheese dyeing is in estimating the shade of the bulk. Some dyers thread a few strands of the yarn to be dyed through cheeses and withdraw one as required for matching, whereas others prefer to take out a cheese and remove some of the yarn from the outer layer of the cheese. The first method is preferable, since an idea of the degree of penetration is also indicated.

Compared with hank dyeing, cheese dyeing is more economical, since in hank dyeing the yarn is wound from the spinner's package into hank and is then usually wound back into cheese for warping, etc., whereas in cheese dyeing winding into hank is eliminated. See also article on the cheese dyeing of worsted yarns ("Wool Record," 1941, pp. 338, 366).

The Hussong Type of Machine.—This machine, which is used for the dyeing of slubbing and yarns, consists of a rectangular wooden dyevessel divided into two compartments ; in the more modern types the dyevessel is lined with acid resisting metal to facilitate cleaning. The largest compartment has a false bottom and contains a removable wooden or stainless steel framework supporting a number of dyesticks carrying hanks packed uniformly so as to avoid channelling of the dyeliquor, and a smaller
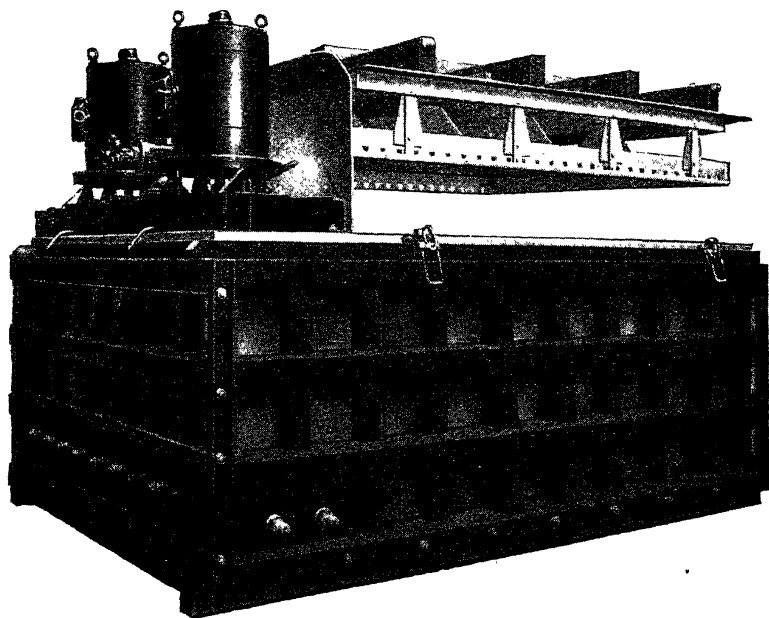

Fig. 12.—Hussong type dyeing machine (Samuel Pegg and Son).

compartment containing one or more propellers to circulate the dyeliquor. The direction of circulation may be reversed and this motion either lifts or straightens the hanks according to whether the dyeliquor is flowing upwards or downwards. Experience has shown that in order to obtain satisfactory dyeings the length of the machine must not be too great or the hanks farthest away from the propellers will be dyed to a paler shade than that obtained on the nearer hanks ; larger machines, therefore, are obtained by increasing the width, and not the length, of the machine.

In using this machine the slubbing or yarn in hank form is

placed on the dyesticks and loaded on to the frame outside the dyevessel ; the loaded frame is then lifted into the dyevessel containing the dyeliquor by means of an overhead crane or similar device, and the frame fastened in position.   The propellers are then started, and the dyeliquor circulated in a downward direction. After a suitable time the direction of flow is reversed and this changing of direction is alternated until dyeing is complete ; in certain cases downward circulation only has been found necessary to give satisfactory dyeings with less danger of entanglement of the hanks.   With slubbing, if the flow of dyeliquor is too strong it may become matted or torn, whilst if the flow is too weak unsatisfactory penetration is probable.   According to Isles (*J.S.D.C.* 1937, p. 420), satisfactory results can be obtained in this machine by piling the slubbing in hank form on the false bottom.   In this way bigger weights can be dyed than by placing the hanks on sticks.

OTHER MACHINES

1. A beam dyeing plant designed by Baldwin and Heap is described in the " Textile Recorder Year Book," 1940, p. A244.

2. A continuous loose cotton dyeing machine constructed in the U.S.A. by J. Brandwood is described in *J.S.D.C.*, 1934, p. 5. This machine is capable of dyeing loose cotton continuously with direct and sulphur dyestuffs at the rate of half-a-ton per hour and has been adopted by some textile mills of the U.S.S.R.

6

Section V.—BASIC DYESTUFFS

The basic dyestuffs are so called because the actual colouring principle has a basic character derived from the amino groups present in the dyestuff, either as free amino groups or amino groups alkylated in varying degrees usually $N(CH_3)_2$ or $N(C_2H_5)_2$. To ensure good solubility they are generally marketed as the hydrochlorides or as salts of other acids such as oxalates, whilst some are zinc double salts. They are also supplied as free bases for the colouring of oils, fats, and waxes.

To the dyer the basic dyestuffs are one class, but to the chemist they consist of the following classes :

Triphenylmethane	..	..	Magenta (C.I. 676).
Diphenylmethane	..	..	Auramine (C.I. 655).
Acridine	..	..	Acridine Yellow (C.I. 785).
Induline	..	..	Indamine Blue (C.I. 859).
Oxazine	..	..	Meldola's Blue (C.I. 909).
Thiazine	..	..	Methylene Blue (C.I. 922).
Azine ..	..	..	Saffranine (C.I. 841).
Azo ..	..	..	Bismarck Brown (C.I. 331).

The resorcine or phthaleine dyestuffs, such as Rhodamine B (C.I. 749), Eosine (C.I. 768), etc., may be grouped with the basic dyestuffs, although they include members which are used not only as basic but also as acid and mordant dyestuffs.

Basic dyestuffs may be applied to textile fibres with or without the use of a mordant (a mordant is a substance which has a chemical affinity for both fibre and dyestuff and, therefore, serves to fix dyestuffs on the fibre). Chemically, the use of basic dyestuffs on textile fibres depends upon their property as bases of combining with acids to form insoluble compounds. Thus Knecht (*Ber.*, 1888, p. 1556) has shown that when wool or silk is dyed with Magenta (C.I. 676) the whole of the hydrochloric acid combined with the Magenta remains in the dyebath at the end of the dyeing

operation, showing that the acid groups of the wool or silk have combined with the colour base of Magenta to form the dyed wool fibre. Jute and related fibres, and vegetable tanned leather, which contain acid groups capable of combining with the colour base can also be dyed with basic dyestuffs without previous mordanting. In the case of jute the direct affinity of the basic dyestuffs has been frequently stated to be due to natural tannin contained in the fibre. Parsons (*J. Textile Inst.*, 1939, p. P322), however, considers that this statement is unfounded and suggests that the affinity for basic dyestuffs is related to the presence of lignin since delignified jute has no affinity for these dyestuffs. Vegetable tanned leather possesses direct affinity for basic dyestuffs by reason of its tannin content. The basic dyestuffs also find application on cotton, linen and rayons. As these fibres, with the exception of nitro-cellulose and acetyl-cellulose rayons, contain no acidic groups they have no direct affinity for basic dyestuffs and require mordanting with acidic substances as detailed later in this section (see p. 89). One notable exception is the affinity for unmordanted cotton and viscose rayon possessed by the basic dyestuff Victoria Blue (C.I. 3), which gives heavy shades on these fibres without a mordant. Overbleached cellulose containing the acidic oxy-cellulose is strongly tinted by solutions of basic dyestuffs, a property made use of in detecting this type of oxy-cellulose.

On their introduction the basic dyestuffs met with a ready demand owing to their brilliancy of shade and great strength of colouring power, as compared with the dyestuffs then available. Unfortunately, many of these dyestuffs are not fast to acids, alkalis, stoving, or washing, and are so fugitive to light that dyed material if left uncovered in a mill room during a week-end in summer may be found to have faded. By an after-treatment with about 2 per cent. Auxanine B (phospho-tungsto-molybdic acid), many basic dyestuffs on cotton have a considerably improved fastness to light, but it must be remembered that this treatment lengthens an already long dyeing process. Phospho-tungstic acid also gives an improvement in light fastness, but is not as effective as phospho-tungsto-molybdic acid (see also p. 97). A number of basic dyestuffs on acetate rayon or wool possess better light fastness than on cotton or viscose rayon. Again, no method has

yet been devised of dyeing basic dyestuffs so that the resulting shades do not rub. In addition to this, these dyestuffs are in many instances extremely difficult to dye satisfactorily, owing to the fact that they are liable to yield bronzy results in heavy shades, whilst in pale shades they are liable to dye unevenly owing to their strong affinity for the fibre. The addition of 0·5–1·0 per cent. of Sapamine KW to the dyebath is advantageous since it retards exhaustion of the dyestuff, and in certain cases may prevent bronzing and increase the fastness to rubbing.

From the above remarks it will readily be understood that dyers are only waiting for adequate substitutes of equal brilliancy of shade in other classes of dyestuffs in order to cease using what are always troublesome dyestuffs. The necessary substitutes have, however, not yet been found, though some of the most recent direct cotton dyestuffs approach the basic dyestuffs in brilliancy, at the same time having superior fastness to rubbing and light. Durazol Fast Blue 8GS (a phthalocyanine derivative), Chlorantine Fast Green 5GLL and the Chloramine Brilliant Roses are typical examples. However, the defects of the basic dyestuffs are so well known to the trade that they are accepted as inevitable, and their use for certain shades has become standardized for many purposes, such as ribbons, tie-cloths and certain dress goods, whilst they are still used for export markets, such as the Gold Coast.

APPLICATION

As the basic dyestuffs are not readily soluble the greatest care must be exercised when dissolving them. The best way is to mix the dyestuff into a paste with cold water or with an equal weight of 40 per cent. acetic acid, and, whilst stirring, add boiling water. This precaution prevents dry dyestuff, which may subsequently form semi-tarry balls, floating on top of the boiling water. Pasting may also be done with methylated spirit, in which basic dyestuffs are readily soluble. Condensed or softened water should be used whenever possible ; if only hard water is available the addition of acetic acid is absolutely necessary, and should the water be exceptionally hard, twice the quantity of acetic acid given above should be used. Alternatively, an addition of

sufficient Calgon (Section XVII.) to counteract the hardness of the water may be made. When dissolving Auramine, care should be taken that the water is not above 75° C. or some decomposition of the dyestuff will occur.

The dyestuff solution should never be added directly to the dyebath, but should be filtered through a calico filter or fine mesh sieve in order to prevent any undissolved particles of dyestuffs entering the dyebath. Such particles quickly attach themselves to the material being dyed and cause specks which may subsequently only be removed with the greatest difficulty—if at all.

Silk.—The basic dyestuffs have a strong affinity for pure silk giving very brilliant shades, so that they are largely used for fabrics, such as ribbons, dance frocks, etc., where light fastness is a secondary consideration. They are applied from a dyebath containing " boiled-off " liquor just broken with acetic acid, or 2–5 per cent. acetic acid alone ; this prevents too rapid exhaustion of the dyebath and consequently assists in obtaining level dyeings. Should only hard water be available for dyeing, it should be corrected by the addition of acetic acid, or Calgon sufficient to counteract the hardness of the water, any scum which floats on the dyebath being removed before the silk is entered. Dyeing is begun cold, the silk worked 15–20 minutes and the temperature of the dyebath gradually raised to 90° C. when the silk is lifted out and washed off. If trouble is experienced in obtaining level results all the dyestuff solution should not be added at the beginning, but the following procedure should be adopted. One-third of the dyestuff solution is added, the silk worked in the cold dyebath until most of the dyestuff has been absorbed, half of the remaining dyestuff solution added and the silk again worked in the cold dyebath until most of the additional dyestuff has been absorbed ; finally, the balance of the dyestuff solution is added and the temperature of the dyebath gradually raised to 90° C. If the silk is to be scrooped after dyeing (*i.e.* passed through a cold weakly acid bath, wrung out and dried without rinsing) it should be remembered that the shade of many basic dyestuffs is changed by weak acid, so that allowance must be made for this change when dyeing to pattern.

If dyed silks are required fast to water they are frequently submitted to the water test, which consists in placing them in

contact with undyed silk and steeping in cold water overnight. The dyestuff must not stain the water or bleed on to the adjacent material. Basic dyestuffs are by no means fast to this test, but their fastness may be considerably improved by the following after-treatment. The dyed material is worked for 15 minutes at 60° C. in a bath containing 2–5 per cent. tannic acid, calculated on the weight of the silk ; allowed to remain in the cooling bath for $1\frac{1}{2}$–2 hours, or overnight, wrung out evenly, and the tannic acid fixed by working for $\frac{1}{2}$ hour in a cold bath containing 1–2 per cent. tartar emetic ; the material is then well washed and dried. This treatment, known as back-tanning, has a dulling effect on the shade so that due allowance should be made when dyeing to pattern ; a colourless tannic acid should be used in order to reduce the dulling to a minimum.

Wool.—The basic dyestuffs are mainly applied to wool yarns, but even here they are of little importance owing to the very large range of other classes of dyestuffs, notably acid dyestuffs like Acid Magenta, Acid Violets, Acid Greens, etc., which enable the wool-dyer to get the same brilliant shades with more easily applied and faster to rubbing dyestuffs. All basic dyestuffs cannot, however, be substituted by members of other classes of dyestuffs. Thus the use of Victoria Blue—despite its marked fugitiveness to light—still continues on loose wool and knitting yarns, because it yields sky to royal blue shades of good fastness to milling, washing, and stoving, which cannot be equalled in brilliancy by any other dyestuff. Again, Rhodamines are also used in the dyeing of wool yarns for knitwear and blanket headings.

Basic dyestuffs may be applied to wool from a neutral dyebath without any addition, but if soft water is available soap may be used, when brighter shades will be obtained. Hard water should be corrected before use with acetic acid or Calgon, otherwise the dyestuff is liable to be precipitated as a tarry mass, and so produce dye stains on the material which are practically impossible to remove. A small excess of acetic acid facilitates level dyeing, but too large an excess retards exhaustion of the dyebath. The wool is entered cold, worked cold for 15–20 minutes, and the temperature of the dyeliquor gradually raised to 90° C. when the dyebath will be found to be practically exhausted. If difficulty

is experienced in getting level shades the precautions detailed under " Silk " (p. 85) should be taken. Unlevel and off-shade dyeings can in most cases be stripped down for correction by treatment in a fresh bath with 1 c.c. per litre of 40 per cent. acetic acid. As Victoria Pure Blue will dye wool in a similar manner to acid dyestuffs it is usually dyed in this way, and not as detailed above.

A special use of Methyl Violet (C.I. 680) may be mentioned here, viz., its use as a blueing agent after wool has been scoured or bleached. A minute percentage is used in order to correct any yellow tone of the wool and thus improve its colour. This operation is sometimes termed a " false bleach," and is usually carried out in a soap bath. The small quantity of perfectly dissolved dyestuff, methylated spirit sometimes being used as the solvent, is added to the soap bath, and the bath well stirred. Any scum appearing on the surface of the soap bath must be removed before the goods are entered, otherwise there is danger of flecky results being obtained.

Jute.—For the purpose of dyeing with basic dyestuffs, coir fibre, piassava, sisal, straw, and wood chip may be classified with the jute. Owing to the fact that lignin enters into the constitution of jute, the basic dyestuffs have a strong affinity for this fibre without any premordanting. These dyestuffs are of primary importance in the dyeing of jute, because being a cheap fibre, cheapness coupled with brilliancy of shade is a governing factor in its dyeing, whilst fastness is of secondary importance in the classes of jute goods for which the basic dyestuffs are used. The dyeing of jute on the big scale is carried out in a quick and simple manner, because the prices paid for dyeing do not admit of any undue amount of labour and time being expended. For most work it is customary to dye without any previous scouring or bleaching unless particularly bright and clear shades are required. Dyeing is usually done with the addition of alum or acetic acid, by adding the dyestuff solution to the lukewarm dyebath, working the jute for 20–30 minutes, and then raising the temperature to 70°–80° C. during 30 minutes. Alum gives the heavier and usually brighter shades, but shades dyed with acetic acid are generally faster to rubbing. For many classes of work, especially yarns which are subsequently made into cut pile goods, it is essential that the jute

should be well penetrated, or "hearted" as the trade terms it. Many basic dyestuffs, notably Methyl Violet and Bismarck Brown do not penetrate well, and so should be avoided in compound shades. In such compound shades as a bronze green produced with Auramine, Bismarck Brown, and Malachite Green (C.I. 657), the substitution of Chrysoidine (C.I. 20) for Bismarck Brown gives a much better penetrated dyeing owing to the better penetration of the Chrysoidine. As poor penetration is the result of too rapid exhaustion of the dyeliquor it follows that unless precautions are taken to slow down the rate of absorption unlevel and badly penetrated dyeings will result. This may be accomplished by the use of cation-active substances such as Sapamine KW or Peregal OK in the dyebath, which result in an improvement in levelness and fastness to rubbing.

As the dyeing literature contains few references to the dyeing of jute the following papers are particularly useful to those interested in this branch of dyeing : " Chemistry in the Processing of Jute," H. L. Parsons, *J. Text. Inst.*, 1939, p. P311 ; " The Dyeing of Jute," D. Carter, *ibid.*, p. P328.

Leather.—Vegetable tanned leather, due to the presence of tannin bodies used in the tanning process, has a direct affinity for the basic dyestuffs ; chrome-tanned leather, on the other hand, requires to be given a preliminary treatment with Sumac—1–2 lb. per dozen skeins—for $\frac{1}{2}$ hour at 50° C. An excess of Sumac should be avoided as it reduces the elasticity and strength of the leather. Recently, the I.C.I. and G. S. J. White (E.P. 416,016) have suggested the mordanting of chrome-tanned leather with an acid of the phosphotungsto-molybdic type containing either molybdenum, tungsten, or both. Leather is usually dyed in rotating barrels or drums. The skins are first worked for a short time with acetic acid only (1 lb. per 10 gallons water), the dyestuff solution then being added in several lots at intervals to the dyebath to prevent the dyestuff from striking rapidly and unevenly. Phosphines are amongst the most popular basic dyestuffs for leather and are used as the basis for most tan shades.

The basic dyestuffs are largely used in leather dyeing, but their use is more restricted than it otherwise would be owing to the fact that they, as a class, tend to exaggerate scratches and grain faults by dyeing these a deeper shade. This is due in part

to the fact that the basic dyestuff is precipitated by any loose tannin in the dyebath as an insoluble colour lake which is absorbed by the flesh side of the skin and those portions where the grain is damaged. By fixing the excess tannin with antimony or titanium salts this is minimized. A more recent process (Lamb and Roche, *J.S.D.C.*, 1933, p. 105) recommends treatment of the leather with an amount of copper sulphate equal to the amount of dyestuff to be used, which gives heavier, more regular, and clearer shades. The importance of these dyestuffs for leather dyeing has been reduced owing to the use of coloured nitro-cellulose lacquers, which when sprayed on to the leather give more uniform results and enable cheaper leather to be used, since local faults are more easily hidden by spraying with such lacquers.

Cotton.—The basic dyestuffs may be applied to cotton by several methods, viz :

(*a*) On a Turkey Red Oil mordant ;

(*b*) With alum and soda ash in a single bath ;

(*c*) On a tannin mordant ;

(*d*) On a Katanol O, Resistone OP, or Taninol BM mordant ;

(*e*) On a pre-dyeing of other classes of dyestuffs which serve as mordants.

Methods (*a*) and (*b*) may be dismissed in a very few words because they are of strictly limited application owing to the shades rubbing very badly, and being very loose to washing ; brilliancy of shade is their only recommendation.

Method (*a*).—The cotton is treated in a cold bath containing 1 part Turkey Red Oil to 10 parts of water, wrung out, dried, and then treated in a 0·5 per cent. solution of soda ash. These operations are repeated once or twice. Alternatively, the cotton may be treated for 20 minutes at 40° C. in the Turkey Red Oil bath, wrung out, dried and then treated for 30 minutes at 50° C. in a bath containing 1 lb. of aluminium acetate (77° Tw.) to every 4 gallons of water and finally well washed. Cotton mordanted by this method may be dyed with Rhodamine to give oil finish pinks which are used for pyjama stripes.

Method (*b*).—The cotton is entered into a bath at 90° C. containing the requisite amount of dyestuff, 10 lb. of alum, and 1½ lb. soda ash, the steam is shut off and the cotton worked to shade and dried without rinsing. The bath is not exhausted, and should

be kept for subsequent lots, when only half the quantity of dyestuff and assistants will be required. It will be recognized that this is not really a dyeing operation, but consists of merely painting the dyestuff on to the fibre.

Method (c).—The method of dyeing on a tannin mordant is a common method of applying the basic dyestuffs to cotton, but is not popular with dyers, as it is slow and entails much labour. Briefly, it consists of mordanting the cotton with tannin and fixing the latter with a suitable metallic salt. The tannins which may be used are tannic acid, sumach, or myrabolans, but unless the two latter have been specially decolorized it is not advisable to use them for pale shades, as their natural dark colour will flatten the dyed shade.

Great care must be exercised in the amount of tannic acid used, because too little mordant does not exhaust the dyebath, whilst excess of mordant, in addition to being a waste of material, causes the dyestuff to rush on the fibre, thus giving uneven results ; moreover, an excess of tannin causes the resulting shade to be dull and lifeless. It is always advisable, therefore, to determine by experimental dyetests the amount of tannic acid requisite for a given dyestuff in given percentages. The following table indicates the average amounts required :

Percentage dyestuff	Percentage tannin	Percentage tartar emetic
0·1	$\frac{1}{2}$	$\frac{1}{4}$
$\frac{1}{4}$	1	$\frac{1}{2}$
$\frac{1}{2}$	$1\frac{1}{2}$	$\frac{3}{4}$
1	3	$1\frac{1}{2}$
$1\frac{1}{2}$	5	$2\frac{1}{2}$
2	8	4

Mercerized cotton and rayon, owing to their greater affinity as compared with ordinary cotton, may be mordanted with less amounts.

The strength of commercial sumach and myrabolans varies considerably, so that depending on the quality, from 2 to 4 times as much is required as compared with tannic acid. As iron reacts with tannins to form ink the presence of iron in the water, or iron in the construction of the bath or steampipe must be rigorously avoided or the shade will be dulled. For this reason

vessels fitted with copper or stainless steel steam pipes are commonly used.

Although tannic acid is absorbed most readily by cotton at 40° C. it would obviously be absurd to enter a tightly twisted yarn into a tannin bath at the temperature of maximum affinity, because under such conditions the mordant would exhaust on to the outside and never penetrate into the centre of the yarn, with the result that it would subsequently only be surface dyed. So that in practice to ensure thorough penetration the yarn is entered into a boiling bath containing the requisite amount of tannin, and worked for 10–20 minutes at this temperature. The steam is then shut off, the yarn immersed under the liquor and allowed to steep overnight. In the morning the yarn is lifted out, wrung out evenly and then fixed without washing, as detailed later. Too much stress cannot be laid upon the necessity for even wringing out, as otherwise the final dyed result will be uneven despite the most careful working in the later stages.

It is obviously not possible to mordant cotton pieces in this manner. This is usually done on a padding machine or in a jigger, and after the pieces have been thoroughly impregnated with tannin solution, they are batched on a roller and allowed to stand 1–2 hours before being fixed. The bath is not exhausted, so that it may be kept and replenished for subsequent lots with four-fifths of the original amount of tannin used. Pieces batched on rollers should not be allowed to remain for long in one position, but the position of the roller should be altered so that there is no possibility of draining of the liquor to the bottom half of the piece ; alternatively, the rollers should be kept rotating.

Tannin treated material should never be put into work unless it can be fixed without having to leave the material lying about, say during the dinner hour, because if it is left unfixed uneven results are inevitable. The authors have investigated more than one case where uneven results have been caused by throwing yarn on top of the bath and allowing it to drain during the dinner hour without wringing the yarn out. Once the tannin has been fixed there is not the same necessity for these precautions, though the quicker the mordanted material is dyed the better the results obtained, because the least trace of iron—even from the condensed steam of the roof of the dyehouse—will cause a dark mark to

appear on the cotton. If goods do get so stained with iron, the stains may be easily removed by working the material in a dilute solution of oxalic or sulphuric acid. If the material cannot be immediately dyed after mordanting, then it should be left covered over with a damp cloth. Sometimes uneven results in dyeing are caused by allowing the mordanted material to lie about so long before dyeing that decomposition of the mordant occurs ; the best remedy in such a case is to remove as much of the mordant as possible with hot dilute sulphuric acid and then to re-mordant.

Cotton treated with tannin alone may be dyed with basic dyestuffs but the results are not as fast—particularly to washing— as those dyed on cotton on which the tannin has been fixed with a metallic salt. For this purpose antimony, tin, aluminium, and iron salts are used in practice. Of these salts, the most commonly used are the antimony salts, tartar emetic ($KSbOC_4H_4O_6$) and antimony salt ($SbF_3(NH_4)_2SO_4$), since these salts give the fastest results to washing ; 9 parts of antimony salt are equivalent to 10 parts tartar emetic. Fixing is done by working the tannin impregnated material in a cold bath for half-an-hour. The material is then thoroughly washed to remove all loosely adhering particles of antimony tannate which would cause the colour to rub ; a light soaping is sometimes also given to minimize rubbing.

Method (d).—In 1921 a new mordant for basic dyestuffs was marketed by the Bayer Co. under the name of Katanol O. This product is a sulphur containing body obtained from o-chlorophenol, sulphur and caustic soda (E.P. 173,313). Similar British products are Resistone O (Glover Bros.) and Taninol BM (I.C.I.). These products possess an affinity for vegetable fibres so that the treated material may be washed off instead of wrung out and fixed as in tannin mordanting ; since no fixing treatment is necessary the long process of applying the basic dyestuff to tannin-mordanted cotton is considerably shortened. Again, unlike tannic acid, which is turned black by iron, these products are not sensitive to metals.

In general, the shades obtained compare very favourably in brightness with those obtained with good quality tannic acids, whilst the washing fastness is better and the light fastness equally as good. When dyeing basic greens and green-shade blues the

yellowish colour of the mordant has an influence on the shade
for which allowance must be made when dyeing to pattern.   In
some cases more dyestuff, particularly in heavy shades, is required
than when using a tannin mordant, so that preliminary trials
should be made before proceeding to bulk work.   Again, some
dyestuffs have a definitely limited affinity, *e.g.* Rhoduline Sky
Blue 3G will not dye on Katanol to a greater degree than is
represented by a 1 per cent. shade, irrespective of the amount of
mordant used or of dyestuff added to the dyebath.

Certain sulphonated triphenylmethane dyestuffs such as Acid
Violet 4BNS (C.I. 695), Disulphine Blue AS (C.I. 714), and
Disulphine Green BS (C.I.677) also have a better affinity for fibres
mordanted with these substances than for tannin mordanted
fibres.   These acid dyestuffs are more soluble and less liable to
bronze than the basic dyestuffs, and so should be used in all cases
if the shade permits.

According to Liepatoff (*Textilber*, 1930, p. 855) commercial
Katanol O is a mixture of free acid and the substantive sodium
salt and its aqueous solution is a colloidal solution of the free acid
and its sodium salt.   Consequently when dissolving Katanol O or
Taninol BM it is necessary to add 10 per cent. of their weight of
soda ash in order to get a clear solution ; with Resistone O the
necessary alkali is already present.   The soda ash is dissolved in
boiling water and the mordant sprinkled in, or the mordant may
be pasted with cold water, the already dissolved soda ash added
and boiling water added to the paste.   The solution should be
yellowish-brown in colour and free from sediment.

These mordants are applied in the same manner as the direct
cotton dyestuffs with the addition of common salt or Glaubers
salt in as short a liquor ratio as possible.   The goods are entered
at 90° C. to ensure thorough penetration and worked in the cooling
bath until the temperature has fallen to 60° C. at which tempera-
ture the mordant has maximum affinity.   From 2–6 per cent. of
mordant is required depending on the depth of shade being dyed ;
as the bath is by no means exhausted it may be retained when
local conditions permit and brought up to strength for further
use.   After mordanting the material is rinsed, a little acetic acid
(1 per cent.) being added to the rinsing water so that no soda ash
may be carried into the dyebath, as this has a detrimental effect

on many basic dyestuffs, *e.g.* Malachite Green, when applied from a neutral dyebath.

Owing to their substantive affinity for vegetable fibres these mordants may be applied in the same dyebath as direct cotton dyestuffs, and the shade subsequently topped with basic dyestuffs as required. By this means, if the shade permits of their use, heavy shades may be obtained more quickly, more conveniently and, therefore, more cheaply than by the use of basic dyestuffs alone.

Method (e).—The basic dyestuffs have an affinity for both the direct cotton and sulphur dyestuffs which results in co-precipitation when their solutions are mixed so that they must never be used together in the same dyebath. Advantage is, however, taken of this affinity by using the basic dyestuffs for topping shades bottomed with direct cotton or sulphur dyestuffs in order to get brighter shades than is possible with these dyestuffs alone. It is also a common practice to top direct cotton blacks with 0·1 per cent. Methylene Blue 2B to counteract any redness of tone, *i.e.* to vivify the shade. Any direct cotton dyestuff may be topped with basic dyestuffs but, as it is usual to top from a slightly acid dyebath, those direct dyestuffs which are sensitive to acids should be avoided. When bottoming with sulphur dyestuffs it is, of course, essential to wash thoroughly prior to topping the bottomed material in order to remove the alkali and sulphide as completely as possible.

Dyeing.—The rate of dyeing of the basic dyestuffs is retarded by an addition of acid or an acid-reacting salt to the dyebath, so that it is customary to make additions of acetic acid or alum to facilitate the production of level and well penetrated shades. In order to assist in obtaining satisfactory dyeings with those dyestuffs which present levelling difficulties it is advisable to first work the cotton in the cold dyebath containing 1–5 per cent. of alum or acetic acid only ; the actual quantity depending on the depth of shade to be dyed. One-third of the dyestuff solution is then added and the cotton worked for $\frac{1}{4}$ hour cold ; half the remaining dyestuff is then added and the cotton again worked $\frac{1}{4}$ hour; finally, the balance of the dyestuff solution is added, the cotton entered, and the temperature gradually raised to 60° C. in $\frac{1}{2}$ hour after which the cotton is washed off and dried. The rate

of dyeing of basic dyestuffs can also be retarded by the addition to the dyebath of cation active substances, *e.g.* Sapamine KW ; an addition of 0·5–1·0 per cent. of this substance being sufficient for this purpose.

In some cases basic dyeings are back-tanned, a process which consists in passing the cotton after dyeing through the previously used mordanting and fixing baths without replenishing them. Despite the length of the process, it is, however, employed for shades which have to withstand a severe milling or cross-dyeing, *e.g.* the bright shades which are to be used as checking threads in cloth which will be subsequently heavily milled or cross-dyed. Whilst all basic dyestuffs are more or less improved by back-tanning, it is most advantageous with the following dyestuffs :

Auramine O (C.I. 655).	Rhoduline Sky Blue 3G.
Brilliant Green Crystals (C.I. 662).	Methylene Blue (C.I. 922).
Malachite Green Crystals (C.I. 657).	Saffranine (C.I. 841).
Brilliant Rhoduline Blue R.	Victoria Blue (C.I. 3).

Rhoduline Yellow 6G.

The dyed cotton is worked in the cold tannin bath for $\frac{1}{2}$ hour, wrung out or hydro-extracted, worked $\frac{1}{4}$ hour in the cold fixing bath and then finally well washed off. This additional treatment further lengthens an already long dyeing process, but has the advantage of improving the fastness of shades to perspiration, washing, milling, cross-dyeing and sometimes gives a slight improvement in light fastness. As back tanning results in a dulling of the shade an allowance for this effect must be made when dyeing to pattern.

Rayons.—The use of basic dyestuffs on regenerated cellulose rayon is to be deprecated as the long dyeing process is very detrimental to the condition of the rayon. Partial blinding and a harsh handle frequently result, whilst the shades, as on cotton, are fugitive to light and often rub badly. It must be recognized, however, that the trade demands certain shades which can only be obtained by the use of basic dyestuffs so that the dyer is still compelled to use them.

Nitrocellulose rayon differs from viscose and cuprammonium rayons in possessing a strong affinity for basic dyestuffs without

the aid of a mordant. It is true that these dyestuffs may be applied to the latter rayons without a mordant if the shades are not too heavy, but this procedure is not to be recommended as the resulting shades are even more fugitive than those dyed on a mordant. The mordant used may be :

(*a*) Direct cotton dyestuff.
(*b*) Katanol, Resistone, and Taninol.
(*c*) Tannin.

Basic dyestuffs dyed from an acetic acid bath on rayon bottomed with a suitable direct cotton dyestuff are quite good, but the shades obtainable have definite limitations as regards brightness of tone as compared with a shade on Katanol or tannin.

Katanol (Resistone, Taninol), possesses definite advantages over tannin for rayon. Its application (see p. 93) has the great advantage of being a shorter process than that for tannin, whilst it avoids the use of a metallic fixing agent and does not give the fibre the harsh handle that tannin does. It has the further advantage of covering yarn of varying dyeing affinity better than the same dyestuff on a tannin mordant. Moreover, a basic dyestuff dyed by this method, then back-tanned, is faster to the standard perspiration test than a basic dyestuff which is first dyed on tannin mordant and then back-tanned. Its dis-advantage is that it does not always give the same depth of shade from the same percentage of some basic dyestuffs, *e.g.* Rhodamines, as when dyed on a tannin mordant. For the estimation of Katanol and its absorption by viscose rayon, see King and Wadadekar, and Johnson, *J.S.D.C.*, 1928, p. 237.

Unfortunately, the basic dyestuffs strike very unevenly on rayon so that the dyestuffs should always be added to the dyebath in several portions in order to get the best results. This in-evitably means long processing, so that it is not uncommon for the process of mordanting and dyeing together with the subse-quent rinsing to occupy 6 hours. It will be readily understood that it is impossible for the yarn dyer—be he ever so careful—to deliver a satisfactorily winding yarn which has been through so long a process.

If basic dyestuffs are applied from an acetic acid dyebath, the use of cation active substances, such as Sapamine KW,

which are stable to acetic acid, are to be recommended for improving the final handle of the yarn.

Miscellaneous Materials.—The basic dyestuffs find a large application in the dyeing of paper, especially Auramine, Saffranine, Magenta, Methyl Violet, and Malachite Green, all of which dyestuffs have become standardized in the paper trade. They are simply dyed by adding the dyestuff solution to the beater and beating the pulp up until it is uniformly dyed. On the addition of alum and resin size fixation of the dyestuff and sizing of the paper takes place simultaneously.

Basic dyestuffs may also be applied on an appropriate base as tannin-antimony lakes, or dyed on to green earth for the production of coloured lakes which are used in the wallpaper, plastics and paint industries. The importance of these dyestuffs was increased with the discovery by Imerheiser in 1914 (E.P. 15,951). that complex inorganic acids such as phospho-tungstic or phospho-molybdic, etc., or salts of these acids when used as precipitants for basic dyestuffs give lakes of outstanding brilliancy of shade, fastness to water and very good fastness to light. The use of phosphotungsto-molybdic acid gives lakes which are faster to light than those made from phosphotungstic acid. These lakes, which are marketed as Fastel Supra (I.C.I.), Consol (Lewis Berger), etc., colours are considered to be salts of the complex acid, $3H_2O$, P_2O_5 (aWO_3+bMoO_3), in which the hydrogen atoms are replaced by basic dye radicles and where $a+b=18$ or 24. (See also article by Richards, *J.S.D.C.*, p. 378, 1936.)

SECTION VI.—ACID DYESTUFFS

THE acid dyestuffs include the following distinct chemical groups :

Nitro dyestuffs..   ..   .. Naphthol Yellow (C.I. 9).
Mono-azo dyestuffs   ..   .. Fast Red (C.I. 176).
Dis-azo dyestuffs   ..   .. Croceine Scarlet (C.I. 277).
Nitroso dyestuffs   ..   .. Naphthol Green (C.I. 5).
Triphenyl-methane dyestuffs.. Wool Green (C.I. 737).
Xanthene dyestuffs   ..   .. Erio Fast Fuchsine BL (C.I. 758).
Anthraquinone dyestuffs   .. Solway Blue SES (C.I. 1053).
Azine dyestuffs   ..   .. Azocarmine (C.I. 828).
Quinoline dyestuffs   ..   .. Quinoline Yellow (C.I. 801).

More recently the Neolan and Palatine Fast dyestuffs, which are o-hydroxy-azo compounds containing co-ordinated chromium in the molecule (see *J.S.D.C.*, 1934, p. 282), and the Carbolan dyestuffs, acid dyestuffs containing a long paraffin chain in the molecule, have been added to this widely used class of dyestuffs.

All acid dyestuffs are sulphonic acids and are usually put on the market in the form of the sodium salt, though some are marketed as the calcium salt, *e.g.* Disulphine Blue AS (C.I. 714).

Despite their constitutional variety, they are all one class from the dyeing point of view in that they are best dyed from an acid dyebath, and hence the name " acid " dyestuffs. The acid dyestuffs are a most comprehensive range, the individual members of which possess the most varying degrees of fastness to light, milling, stoving, etc., whilst they also vary considerably in their dyeing properties. For example, Soluble Blue is extremely fugitive to light—Solway Blue SES is extremely fast ; Acid Magenta possesses no fastness to milling whilst Elite Fast Orange R is very fast to milling ; Coomassie Navy Blue 2RNS is a poor levelling dyestuff ; Azo Geranine 2GS is a very good levelling dyestuff. It has, however, been shown that acid dyestuffs can be roughly classified into two classes (see Goodall, *J.S.D.C.*, 1935, p. 405) according to their state in solution as follows :

(a) *Molecularly Dispersed Acid Dyestuffs.*—These are considered to dissociate completely in solution into one or more sodium ions and a negatively charged dyestuff ion thus :

$$\text{10NaD} \;\rightarrow\; \text{10Na}^+ \;+\; \text{10D}^-$$

Such dyestuffs are characterized by high solubility, clearness of solution, high capillary rise (see *below*), lack of affinity for vegetable fibres, and by their poor affinity in a neutral dyebath. They are dyed with sulphuric or formic acid in the dyebath, are easily levelling, and possess poor fastness to wet processing. Examples of this class are Xylene Light Yellow 2G, Acid Orange GG, Azo Geranine 2GS, etc.

(b) *Aggregated Acid Dyestuffs.*—In solution these dyestuffs consist of aggregated particles each containing a number of dyestuff molecular equivalents, and their dissociation in water might be represented as follows :

$$\text{10NaD} \;\rightarrow\; \text{3Na}^+ \;+\; [\text{Na}_7\text{D}_{10}]^{---}$$
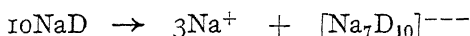
The actual size of the dyestuff particle in solution varies according to the degree of aggregation.

These dyestuffs are characterized by poor solubility, turbidity of solution (particularly when cold), low capillary rise (see *below*) a capacity for staining vegetable fibres, and a distinct affinity for wool when dyed from a neutral dyebath. They may be dyed with ammonium acetate, ammonium sulphate, acetic acid or even from a neutral dyebath, have poor levelling properties, but good fastness to wet processing. Examples of this class are Polar Yellow R. conc., Coomassie Navy Blue 2RNS, Elite Fast Red R conc., etc.

It must be realized that the two classes are not sharply defined but merge into one another.

A very simple method for roughly classifying the acid dyestuffs into these two groups is to determine the capillary rise of the dyestuffs on filter paper (see Garner, *J.S.D.C.*, 1933, p. 346). When one end of a strip of filter paper is dipped into water it rises to a definite height. If an aqueous solution of an acid dyestuff is used instead of plain water the dyestuff rises to a height which depends upon the particle size of the dyestuff in solution. Thus an aggregated acid dyestuff shows only a low rise, whereas

some of the molecularly dispersed dyestuff rises to approximately the same height as the water (see Section XVI.).

The theory of the dyeing of acid dyestuffs on wool has been the subject of a considerable amount of research for many years, but many points of the mechanism of dyeing are still not universally accepted.

It has been established (see p. 21) that wool is an amphoteric protein which, therefore, contains basic groups capable of combining with acids to form salts and that the wool fibre is built up of micelles consisting of long peptide chains linked together by cystine and salt linkages.   Between the micelles are spaces known as inter-micellar spaces.   It is into the latter that dyestuffs must penetrate before dyeing can take place ; this is facilitated by the swelling of the wool when it is placed in water which is increased by acid or alkali addition, or by rise in temperature, but is depressed by the presence of neutral salts, such as Glauber's salt. It was formerly accepted that the acid used in dyeing liberated the free colour acid from the dyestuff, which then combined with the base of the wool substance forming a coloured compound representing the dyed shade.   This mechanism of dyeing was, however, disproved largely as a result of the work of Knecht (*J.S.D.C.*, 1888, p. 107) and Hallitt (*ibid.*, 1899, p. 30).

Fort (*J.S.D.C.*, 1916, p. 33) concludes that the wool base first forms an additive salt with sulphuric acid, and, therefore, the process of dyeing wool with an acid dyestuff may be expressed by the following equation :

Wool Base H_2SO_4+Colour Acid NaSalt
$$\rightleftharpoons \quad \text{Wool Base Colour Acid}+Na_2SO_4$$
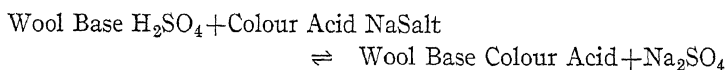
The reaction is reversible, which shows why Glauber's salt may be used as a levelling agent, whilst it also explains the reason why a boiling concentrated Glauber's salt bath will strip many acid dyestuffs from the fibre.   To quote Fort's own words : " Commercial dyeing of acid dyestuffs is mainly dependent on the use of a free acid in conjunction with the dye, and the aid thus rendered in dyeing is dependent on the chemical reaction between dye and the acid fibre compound formed initially and not, as hitherto supposed, as a process of liberation of free colour acid in the bath."

More recent work by Astbury, Speakman, Porai-Koschitz, and Elöd appears to show that Fort's theory of the mechanism of dyeing in an acid dyebath is basically correct. Thus Elöd (*Trans. Faraday Soc.*, 1932, p. 327) has shown that on immersing wool in an acid dyebath the acid is first of all absorbed with formation of the protein salt of the acid. This is followed by replacement of the acid by the dyestuff anion with formation of the protein salt of the dyestuff. Elöd's graph of the process of wool dyeing with Crystal Ponceau R in a hydrochloric acid dyebath at 50° C. liquor ratio 50 : 1 illustrates this, as is shown.

A = pH.   B = pCl.   C = Dyestuff taken up.
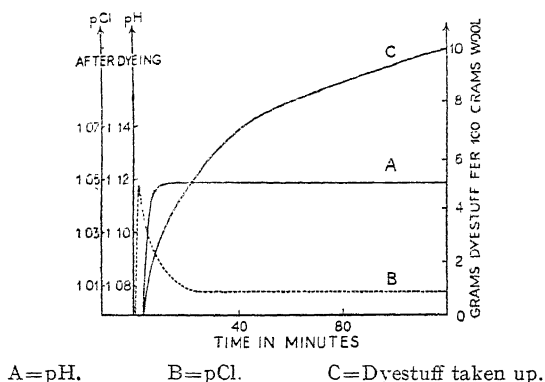
This mechanism of dyeing has been shown to be capable of explanation by Donnan's theory of membrane equilibrium (see Goodall, *J.S.D.C.*, 1937, p. 50, who has therein summarized the recent work on the theory of wool dyeing). These results can only be expected from a chemical theory of dyeing. Such a theory has received some confirmation from Speakman and Stott's demonstration that de-aminated wool has a much reduced capacity for combination with both acid or dyestuff, and that the remaining capacity is possibly due to imino groups (*J.S.D.C.*, 1934, p. 341).

The above mechanism of dyeing gives a satisfactory explanation of the properties and behaviour of dyestuffs which are in molecular solution, and which give an ion capable of diffusing not only into the inter-micellar spaces of the wool fibre, but also into the micelle itself. There is such a marked difference in behaviour between characteristic molecularly dispersed and

aggregated dyestuffs respectively that it seems difficult to apply the same theoretical conceptions to both types.

The aggregated dyestuffs, although small enough to enter into the inter-micellar spaces of the wool fibre, unlike the molecularly dispersed dyestuffs, are not small enough to enter readily into the micellar structure itself. Goodall (*J.S.D.C.*, 1935, p. 405) has suggested a mechanism of dyeing whereby such molecular aggregates are " fixed within the fibre." In this theory it is suggested that the smaller Na cations penetrate into the micelle and exert a constant attractive force on the dyestuff anions which are thereby drawn into the fibre micelle until they are prevented by their own actual size from proceeding further in the narrow space available. This theory, therefore, assumes that the aggregated dyestuff particles are held in position by a purely electrostatic attraction, which, in conjunction with the shrinking of the fibre on cooling and drying, can account for the high wet fastness and other properties of the group. On the other hand, Valkó (*J.S.D.C.*, 1939, p. 173) has suggested that even characteristic aggregated dyestuffs do not form aggregates of more than 2–3 molecular equivalents at the usual dyeing temperature of 100° C. Valkó suggests that the same forces within the dyestuff structure which cause it to aggregate in cool solutions also account for the fastness of the fibre-dyestuff complex.

APPLICATION

The application of the acid dyestuffs is so relatively simple that they are naturally consumed in large quantities, since dyers rightly use them wherever possible. They are largely used in the following branches of wool dyeing; ladies' dress goods, piece dyed gentlemen's suitings and coatings, bathing suits, knitting and hosiery yarns, carpets, furnishings, and in hat dyeing ; also for the dyeing of silk.

On the whole the acid dyestuffs are distinctly brighter than the chrome dyestuffs and find considerable use for shading the latter. Certain types of acid dyestuffs also find a very extended application in the dyeing of jute, leather and paper.

Dissolving.—The dyestuff is stirred into a perfectly smooth paste with cold soft water and is then dissolved by pouring boiling

water over the paste and stirring well. If only hard water is available it should be corrected by the addition of a small amount of acetic acid or Calgon. Amongst the acid dyestuffs the solubility of individual members varies considerably, so that the above instructions are superfluous for those which are freely soluble. At the same time it is advisable as a matter of dyehouse routine to stir every dyestuff into a perfectly smooth paste with cold water before adding boiling water. Such a procedure will prevent undissolved dyestuff from getting unobserved into the dyebath and so causing specks on the material, which are subsequently difficult to remove.

Assistants Used.—Sodium sulphate, usually in the form of Glauber's salt, is generally added to acid dyebaths when using the level dyeing acid dyestuffs because it retards the rate of dyeing of these dyestuffs, and thus helps to prevent the dyestuff from rushing on to the fibre. It, therefore, fills the role of a levelling agent. With the unlevel dyeing acid dyestuffs, *e.g.* Coomassie Navy Blues, Glauber's salt tends to accelerate the rate of dyeing and should be omitted.

The acids which are commonly used are sulphuric, formic, and acetic acids, whilst in special cases salts from which acid is liberated during dyeing may be used, such as ammonium sulphate and ammonium acetate. Of the above three acids sulphuric acid is most commonly used owing to its cheapness, and finds its main application in dyeing the level dyeing acid dyestuffs and for completing the exhaustion of dyebaths which have been started with the addition of acetic acid. Formic acid is of practically equal power to sulphuric acid, but has the big advantage that less acid is retained by the wool after dyeing and that its tendering action on any cotton or viscose rayon present is less severe than that of sulphuric acid. This is a great advantage because it is impossible in practice to wash out all acid from acid dyed goods. If possible, formic acid should, therefore, be given preference when dyeing wool pieces containing cotton or viscose effect threads. In this connection, it should be noted that the temperature of drying of such pieces has a great influence on the tendering of the effect threads ; to minimize tendering, the pieces should not be dried at too high a temperature. Acetic acid is a considerably weaker acid than sulphuric or formic acid and is

used when dyeing the more unlevel dyeing acid dyestuffs which require to be dyed in a weakly acid dyebath, or when dyeing goods which are difficult to penetrate, since dyeing proceeds more slowly with acetic than with sulphuric or formic acid. Ammonium acetate or ammonium sulphate may be used instead of acetic acid when dyeing the unlevel dyeing acid dyestuffs, since when boiled, their solutions slowly develop acidity and so prevent unlevelness caused by rapid exhaustion of the dyebath.

DYEING

Wool.—The dyeing of wool may take place at four different stages of its manufacture, viz. :

1. Loose wool.
2. Slubbing (Tops).
3. Yarn.
4. Piece.

The particular stage at which wool is dyed depends upon the quality and class of goods into which it is to be manufactured ; thus it is essential for goods showing a mixture effect to dye the wool in the loose form or as slubbing, from which the mixture effect may be obtained by blending. Wool for carpets is dyed either in the loose form, or more generally as yarn, whilst a large proportion of knitting yarn is also yarn dyed. The majority of ladies' goods and the cheaper qualities of men's goods, as well as blacks, browns, and blues in the best qualities, are dyed in the piece. Dyeing in the piece is the cheapest method and is adopted whenever circumstances will permit, whereas dyeing in the loose form or as slubbing is the most expensive, but gives the best results in respect of both levelness and penetration, since the individual fibres are more thoroughly penetrated than is mechanically possible with wool in the form of yarn or piece. Owing to the better penetration obtained by loose wool dyeing more dyestuff is usually necessary to give the same shade than is required in piece dyeing.

With the exception of slubbing, which is usually dyed "in the oil," that is, 3–5 per cent. oil from the combing is not washed out before dyeing, it is essential that the wool be efficiently scoured so that the dyestuff may not be prevented by grease from penetrating the fibre (see p. 42).

Loose wool is dyed in open vats of iron, copper, wood, monel or stainless steel, or in one of the many forms of loose-wool dyeing machines. As the majority of shades dyed in this form are intended to undergo subsequent milling, dyestuffs of good milling fastness are usually employed. Slubbing may be dyed in hank form in an open beck, although nowadays it is almost entirely dyed in machines. The most widely used machine for slubbing dyeing is undoubtedly the Hussong machine, although the Longclose cylinder or can type, Obermaier and Klauder-Weldon machines are also used. It is dyed both in fast milling shades, similar to those on loose wool, and also in less fast shades for knitting yarns. Yarns are dyed by hand in open becks, or in machines of the pack or Hussong type. Since dyed yarns have to be wound into cheeses prior to warping, a certain amount of wool yarn is dyed in the cheese form on the pack system. This is particularly suitable for singles yarn ; the newer auxiliaries have made the scouring of wool in package form possible. Wool yarns are used for such a variety of purposes that they are dyed with dyestuffs of all degrees of fastness ; with level dyeing acid dyestuffs for hand knitting yarns and carpets, etc. ; with faster members of the level dyeing acid and milling dyeings for bathing costumes, etc.

In piece-dyeing the winch machine is universally used, the pieces being sewn together and drawn over the winch and through the liquor. The machine should be fitted with a reversing gear so that the winch can be turned in either direction in case the pieces become entangled, etc. Pieces having tightly woven lists which curl badly should be sewn together at intervals of 3–6 in. with the face side inwards and dyed in tubular form. This is commonly known as " bagging." Dark lists can usually be avoided by letting the pieces run in rope form and changing the position of the folds by occasional poling. When the pieces are dyed to the required shade they should be run through a tank of cold water, plaited down, and unless they are to be tentered immediately the precaution taken to wrap them up in the tail of the piece to keep them clean.

In dyeing the average level dyeing dyestuff the dyebath, in which there is about 1 ft. of water, is charged with the requisite quantity of previously dissolved dyestuff and boiled for 10 minutes,

after which it is filled up to working level with cold soft water, Glauber's salt and any necessary acid added and thoroughly stirred with a rake.   Another method is to put the dyestuff in a cotton bag and boil the bag in the dyebath till all the dyestuff is dissolved.   The material is then entered at about 40° C., worked 10 minutes, steam turned on, and the bath brought to the boil in $\frac{1}{2}$ hour and dyeing continued at the boil until the required shade is obtained.   3–5 per cent. sulphuric acid (96 per cent.) and 10–20 per cent. Glauber's salt are used for the easily levelling type of acid dyestuff, but several alternative methods may be employed depending upon the actual dyestuff used and on the type of material to be dyed; thus, in yarn dyeing 4 per cent. sulphuric acid is often employed irrespective of the depth of shade.   The modifications which may be made are given below, but their adoption in suitable cases must be left to the discretion and experience of the individual dyer.   If the dyestuffs are extremely easy-levelling like Xylene Light Yellow 2G, the material may be entered into the dyebath at a much higher temperature, and no time need be wasted in raising the dyebath to the boil.   On the other hand, with dyestuffs such as Coomassie Red PGS which show a tendency to rush on to the fibre, it is the usual practice for dyeing to be started at a low temperature with acetic acid instead of sulphuric acid or even without acid to prevent the too rapid exhaustion of the dyebath. Alternatively the Goodall method (see p. 107), which offers particular advantages with dyestuffs of this type, may be used.   It is undesirable in practice, but sometimes necessary in order to secure complete exhaustion, to make further additions of acid towards the end of the dyeing.

Wool pieces containing cotton or rayon effect threads which have to be left unstained, require to be dyed in a strongly acid dyebath so that the level dyeing acid dyestuffs are particularly suitable for this type of work.   Formic acid is often used for this purpose because it has not the same tendering effect on the cotton and rayon as sulphuric acid.   Such pieces should be washed off immediately after dyeing, and no time should be lost in drying them ; if left lying about in the wet state, especially under pressure, the wool dyestuff is very liable to bleed on to the previously clean effects and stain them.

If difficulty is experienced in getting the dyestuff to penetrate

thick cloths or tightly twisted yarns, then use is made of ammonium acetate made by mixing 4 parts ammonia (24 per cent.) with 10 parts acetic acid (30 per cent.). This will be slightly alkaline to litmus, which is no disadvantage when it is being used for dyeing. As the bath gets hot the ammonium acetate splits up into ammonia (which boils away) and acetic acid. The result is that the bath becomes slowly acidified, so that dyeing proceeds regularly and slowly and the dyestuff is prevented from rushing on to the surface of the material (see Section VII.). When using ammonium acetate it will usually be found necessary to add acetic acid towards the end of the dyeing in order to exhaust the dyebath.

A method for dyeing the unlevel-dyeing, aggregated wool dyestuffs, involving the use of normal amounts of acid partially or entirely neutralized by ammonia and employing dyebaths free from Glauber's salt, has recently been worked out by Goodall (*J.S.D.C.*, 1938, p. 45). In this method the dyebath is raised to the boil, the steam turned off, ammonia or ammonium sulphate added, and the material entered into the dyeliquor with the steam still turned off. The temperature is then raised to the boil and dyeing continued at the boil until the desired shade is obtained. Bulk trials of this method show much improved results with these dyestuffs as regards levelness, penetration, fastness to rubbing and brightness of shade as compared with dyeings made from the usual acetic acid and Glauber's salt dyebath.

The Coomassie Navy Blues which are unlevel dyeing acid dyestuffs have won for themselves a most important place in wool-dyeing, due to their fastness to light and milling, but their adoption by the dyeing trade was very slow at the outset owing to the many difficulties encountered in their application. This is now thoroughly understood, with the result that these dyestuffs have become standardized for certain classes of goods, especially piece-dyed goods, but their adoption has been limited owing to their liability to turn brown on decatizing.

The following points must be carefully attended to in order to get successful results :

1. The wool must be perfectly scoured and free from grease ; this is, of course, true for all wool dyestuffs, but Coomassie Navy

Blues are particularly sensitive to any grease or soap residues.   If the dyer has reason to doubt the cleanliness of pieces coming to him it is advisable to run them through a weak ammonia bath at 60° C. ; 1 quart of ammonia (880) for 50 lb. of material being sufficient for this purpose.   This will remove any soap residues on the piece.   Dirty pieces, or pieces which have been stored for some time should be chromed before dyeing.

2. Coomassie Navy Blues are sensitive to reducing agents and to hydrolysis.   Thus it is stated that the decomposition of Coomassie Navy Blue takes place in solution most readily under acid conditions, by hydrolysis of the azo group ; on the fibre, most readily under alkaline conditions, by reduction of the azo group by the sulphur in the wool.   It is for this latter reason that improved fastness to steam blowing is often obtained by deliberate souring of Coomassie dyed pieces.   As some of the Coomassie Navy Blue types are extremely sensitive to hydrolysis in acid solution, the high temperature wool dyeing method is of particular advantage with these types, since dyeing is commenced alkaline, *i.e.* when the colour is in solution, and finished slightly acid, *i.e.* when the colour is on the fibre.   Decomposition to a brown can take place in the dyebath, especially if the bottom of the cistern is covered with large perforated iron plates and the authors have come across instances of the wool coming out brown instead of blue due to this cause.   Coomassie Navy Blues are unaffected by boiling with bichrome, so it is always advisable to dye with the addition of $\frac{1}{2}$–1 per cent. bichrome, which immediately oxidises any reducing agent which may be produced during dyeing, yielding brighter shades than if no bichrome is added, especially if dyeing is prolonged.

The dyebath is, therefore, charged with the requisite amount of dyestuff and $\frac{1}{2}$–1 per cent. bichrome, the material entered cold, and the dyeliquor carefully raised to the boil in the course of $\frac{3}{4}$–1 hour.   It is not advisable to have the liquor boiling vigorously, but just simmering.   The dyeliquor is now usually well exhausted, steam is shut off, and $\frac{1}{2}$–2 per cent. acetic acid, 40 per cent. well diluted with water, is added ; steam put on again, and dyeing continued for $\frac{1}{2}$ hour at the boil.   The opinion of dyers is divided on the question of the addition of acetic acid.   Those who do not use acetic acid argue correctly that the danger of uneven

results is much reduced if no acid is added ; on the other hand, it is agreed that the shade is fuller, though less bloomy, if acetic acid is added. In dyeing loose wool, therefore, on which absolutely level results are not of such moment, acetic acid should be added ; when dyeing yarn or piece the use of acetic acid must be left to the discretion of the dyer, but it is safer to omit it even at the expense of some loss of depth. It should be noted that many dyers prefer to use ammonium sulphate instead of acetic acid for this purpose.

Neolan and Palatine Fast Dyestuffs.—The Neolan and Palatine Fast dyestuffs are a series of acid dyestuffs containing combined chromium which have somewhat similar dyeing characteristics to ordinary acid dyestuffs, but which possess fastness properties approaching those of chrome dyestuffs. The fibre-dye complex is only converted into its final state by boiling with a greater percentage of mineral acid and for a longer period than that usually employed for dyeing ordinary acid dyestuffs. This procedure is necessary in order to obtain the correct shade and the best possible results as regards levelling and fastness properties. For this reason the following special method of application is recommended, although in certain cases of dyeing in enclosed machines, *e.g.* with cheeses and slubbing and loose wool, satisfactory results are obtained with less acid owing to the lower liquor ratios employed with such machines.

The dyestuff is dissolved in the usual manner, added to the dyebath at 60°–70° C., and 6–8 per cent. sulphuric acid 96 per cent., suitably diluted, is then added. Usually the acid is added in two portions, one half at the start and the other half after raising to the boil in $\frac{1}{2}$–$\frac{3}{4}$ hour. Dyeing is then continued for $1\frac{1}{2}$ hours at the boil, in order to obtain level results and complete development of shade and fastness. Satisfactory results can also be produced by dyeing with about 5 per cent. sulphuric acid and the addition of 1 per cent. Neolan Salt II or 2–3 per cent. Palatine Fast Salt O to the dyebath just as it reaches the boil. When dyed under correct conditions, these dyestuffs are level dyeing and the shades possess excellent fastness to light, water, perspiration, seawater and wear. They are not as fast to milling as the chrome dyestuffs, but will withstand light milling and scouring. Owing to their ease of application and fastness properties, they are used

for the dyeing of mens' and tropical suitings ; they also find application for the dyeing of high-class dress goods for ladies' wear. This group of dyestuffs have also been found of particular value for the dyeing of hosiery and carpet yarns. With regard to the latter, Neolan dyestuffs have been found eminently suitable for the dyeing of yarns which are to be woven into carpets where the highest standard of fastness to light, washing and salt water are required, *e.g.* train, ship, theatre, and hotel carpets.

Many of the Neolan dyestuffs are dischargeable to a pure white, and on account of this property find extensive application for the dyeing of piece goods which are required to be discharged and manufactured into fancy goods, such as ties, scarves, etc.

An important point in dyeing Neolan and Palatine Fast dyestuffs is the question of rinsing. With the chrome dyestuffs it has been the trade custom to give only a short rinsing after dyeing. This is insufficient when 5–8 per cent. sulphuric acid has been used, as wool has a strong affinity for acid, which can only be removed with difficulty and requires thorough rinsing, preferably with a little ammonia in the last wash water. Neglect of this precaution may result in difficulty with slubbing and loose wool in milling or back-washing and also with piece goods containing cellulosic effects.

Correction of Uneven or Wrong Shades.—Material dyed with acid dyestuffs which is slightly uneven may often be corrected by boiling in clean water with a large percentage of Glauber's salt, if necessary with some undyed material to absorb some of the dyestuff which passes into the dyebath on boiling. If this is not effective strip some of the dyestuff with hot ammonia and a sulphonated fatty alcohol. In still more obstinate cases the shade must be stripped down with a formaldehyde hydrosulphite, such as Hydrosulphite FD conc. with acetic acid addition, after which treatment it is important to run for 20 minutes at 60°–70° C. in a bath containing 2–3 per cent. ammonia, if level results are to be obtained in subsequent re-dyeing. In the case of piece goods dyed with the Neolan and Palatine Fast dyestuffs the method of " licking off " has proved to be successful when the material is dyed too deeply. The faulty pieces are treated with undyed pieces in a fresh bath containing 4 per cent. sulphuric acid and

10 per cent. Glauber's salt on the weight of goods, starting at 65° C. raising to boil and boiling for 1 hour. In cases where this treatment is insufficient stripping with acid Hydrosulphite FD conc. is resorted to.

Silk.—The acid dyestuffs are widely used in silk dyeing to give level dyeing bright shades, many of which have very good fastness to light and are sufficiently fast to washing to satisfy commercial requirements.

These dyestuffs may be applied from a suitably diluted boiled-off liquor bath ($\frac{1}{2}$–2$\frac{1}{2}$ gallons per 10 gallons dyebath) which has been broken with sulphuric, formic, or acetic acid ; sulphuric acid being used for dyestuffs which dye from a strongly acid dyebath.

The dyeing is started at about 38°–50° C., the temperature gradually raised to 90°–95° C. and dyeing continued for $\frac{1}{2}$–1 hour at this temperature. To promote exhaustion of the dyebath a little acid may be added during the dyeing. It is not advisable actually to boil the dyeliquor when dyeing silk, because many acid dyestuffs begin to boil off the fibre at the actual boil. Again, certain dyestuffs such as Rocceline (C.I. 176) have so pronounced an affinity for the silk that they can be dyed equally satisfactorily at a lower temperature than indicated above. The lower the temperature employed the better is the natural lustre of the silk preserved. After dyeing the silk is rinsed and brightened in weakly acidulated water. In piece dyeing the acid dyestuffs may be applied from a dyebath containing 10–20 per cent. Glauber's salt and 1–3 per cent. sulphuric acid by the method described above although it is more usual to use neutral dyeing colours without acid.

When dyeing tin-weighted silk an excess of acid should be avoided owing to its deleterious effect on the weighting. For this reason dyeing is often done from a neutral soap bath. Neutral acid dyestuffs are also widely used and are applied from a Glauber's salt bath at or near the boil, a little acetic or formic acid being used when necessary to assist exhaustion. It must be borne in mind that many acid dyestuffs which will dye unweighted silk satisfactorily possess no affinity for weighted silk due to the tin salt resisting the dyestuffs, whilst some dyestuffs are not as fast to light on tin-weighted silk as on unweighted silk. For

methods of distinguishing tin-weighted from unweightd silk, see p. 37.

The Alkali Blues give very fine bright shades on wool aid silk ; and are still great favourites for the latter fibre.   They require to be dyed in the following manner : Dye at 90° C. for $\frac{1}{4}$ hour with the addition of 1–4 per cent. borax or 1–3 per cent. soda ash, wash and develop for $\frac{1}{2}$–$\frac{3}{4}$ hour at 40°–60° C. ir a bath containing 1–4 per cent. sulphuric acid according to tie depth of shade being dyed.   In the dyebath the shade is ver7 weakly blue, but develops up to a full blue in the acid-develcing bath. This method of dyeing has to be adopted because sulphuric acid precipitates Alkali Blue due to the insolubility of th free colour acid in water.

Jute.—Although many acid dyestuffs are suitable for dyeing jute their use is mainly confined to the cheaper members, such as

Indian Yellow G (C.I. 146)	Orange IV (C.I. 143)
Fast Red A (C.I. 176)	Naphthalene Black 12B (C.I.
Citronine (C.I. 145)	246)
Disulphine Blue A (C.I. 714)	Croceine Scarlet 3B (C.I. 252)
Orange II (C.I. 151)	Coomassie Violet R (C.I. 698)

Soluble Blue (C.I. 707)

They possess several advantages over the basic dyestuffs (see p. 87) since they dye more slowly and, therefore, penetrate or " heart " the jute *etter, giving dyeings which are faster to rubbing.   Their light fastness is better than that of the basic dyestuffs though in this respect as well as regards fastness to water they are still very poor.

Excepting for bright shades, jute is seldom scoured and dyeing is usually done at the boil for 1 hour with 1–5 per cent. acetic acid or alum.   In general, acetic acid gives cleaner shades and alum the fuller shade.   An addition of small amounts of sodium bisulphite to the dyebath is stated to improve the level-ness of certain acid dyestuffs and to give simultaneous brightening of the jute itself (Parsons *J.T.I.*, 1939, p. 311).

The above remarks apply equally to coir fibre, piassava, sisal, straw, and wood chip.

Miscellaneous Uses.—The acid dyestuffs are largely used in the dyeing of unions and the newer synthetic fibres, such as " Rayolanda " X, Casein Fibre, and nylon. They are also used for the dyeing of paper and leather.

Section VII.—TRUE ALIZARINE AND OTHER MORDANT DYESTUFFS.

ALL the dyestuffs dealt with in this section possess the property of forming more or less insoluble compounds with metallic salts, but vary widely in their chemical constitution, thus :

Anthraquinone dyestuffs	.. Alizarine (C.I. 1027).
Monoazo dyestuffs ..	.. Solochrome Yellow Y (C.I. 197).
Disazo dyestuffs ..	.. Chrome Fast Black FW (C.I. 299).
Oxazine dyestuffs ..	.. Gallocyanine (C.I. 883).
Triphenylmethane dyestuffs ..	Eriochrome Azurol B (C.I. 720).
Nitroso dyestuffs ..	.. Gambine (C.I. 2).
Oxyquinone dyestuffs..	.. Alizarine Black (C.I. 1019).
Xanthene dyestuffs ..	.. Coeruline (C.I. 783).

The mordant dyestuffs are marketed in the form of pastes and powders. Some of the former, particularly Alizarine Blues (C.I. 1067), are supplied as the soluble bisulphite compounds since the alizarine dyestuff itself is insoluble in water. On warming the solution to 70° C. the bisulphite compound is decomposed and the insoluble alizarine dyestuff precipitated. This behaviour entails special precautions being taken when dyeing such compounds (see p. 119).

From the dyer's point of view the true alizarine dyestuffs are differentiated from the other mordant dyestuffs in that they will not dye wool without a mordant, whereas the latter dye wool a more or less deep, but usually not a fast shade, without the aid of a mordant. The methods of application of these two types of mordant dyestuffs are, however, sufficiently similar to justify their inclusion in one and the same section.

In the naming of those dyestuffs which may be applied in the same way as the true alizarine dyestuffs there has been a regrettable looseness which is misleading to those not familiar with the constitution of these dyestuffs. For instance, anyone seeing

Anthracene Yellow BN (C.I. 195) for the first time would naturally conclude that it bore at least some chemical relationship to anthracene, whereas it has none, but is a monoazo dyestuff made by coupling salicylic acid with diazotized B-naphthylamine mono sulphonic acid. Again, Acid Alizarine Brown B (C.I. 167) would lead the uninitiated to conclude that it belonged to the alizarine class, whereas it ·has no chemical relationship whatsoever to Alizarine, but is made by coupling metaphenylene-diamine with diazotized ortho-amido-phenol-mono-sulphonic acid.

These dyestuffs are applied to wool and silk, and yield some of the fastest shades obtainable on these fibres ; they are consequently used for the best classes of work when dyeing such fibres. On silk, shades of excellent fastness to boiling soap are obtained which could only be obtained otherwise in this fastness by the use of the vat and azoic dyestuffs. They are also applied to cotton, chiefly by printing.

On wool the shades obtained with the mordant dyestuffs are so much superior in fastness to light that they have displaced all the old dyewoods with the exception of Logwood—which holds its own due to its beauty of shade and to its cheapness—and Fustic, which holds its place as a yellow owing to mordant yellows being the least fast members of this series, there being no true alizarine yellow. With the increasing adoption of single-bath methods, both Logwood and Fustic have, however, lost further ground. Again, Turkey Red (alizarine on an alum mordant) remained for years without a rival as the fastest red obtainable on vegetable fibres. In more recent years Para Red (paranitraniline coupled with B-naphthol) partially displaced it—more particularly on pieces—not on grounds of fastness, but because of its cheapness and ease of application, whilst the introduction of the azoic dyestuffs has also had a major effect on the diminishing importance of Turkey Red. It is to be anticipated that vat reds will sooner or later also rival it, but progress in the production of bright vat reds of good affinity for the fibre has been poor.

APPLICATION

Wool.—The mordant dyestuffs are of the highest importance, and are largely used in the dyeing of all classes of woollen

and worsted goods for which the greatest possible fastness is required, *e.g.* Scotch tweeds, West of England cloths, fine worsteds, etc.

Chromium, usually as sodium or potassium bichromate, is the only mordant used nowadays, whereas when the old dyewoods were in vogue, iron, tin, aluminium, and copper were also largely used. An exception is, however, found in the application of Alizarine Red (C.I. 1034) and Alizarine Orange (C.I. 1033) on an aluminium mordant.

The mordant dyestuffs are applied by the following methods :
1. Chrome mordant.
2. Afterchrome or top-chrome.
3. Metachrome or chromate.

Each of these methods has its advantages and disadvantages, according to the class of work being done.

Chrome Mordant.—This is the oldest of these methods and is chiefly used in the application of the true alizarine dyestuffs. It has the disadvantage that it is a two-bath method thus involving more labour, steam, time, and water—cost factors which modern trends in dyeing are always striving to reduce. Nevertheless, dyers still favour the use of a chrome mordant for certain classes of loose wool, though the introduction of new and faster dyestuffs suitable for the other methods is reducing its use. It is also easily the best method for obtaining level results with fancy shades on yarns and pieces. Like the metachrome process, partial development of the final shade takes place almost as soon as the dyebath is raised to the boil and if a new shade is being dyed it is possible for a dyer to satisfy himself that his shade is reasonably correct at an early stage of the dyeing. For the less difficult fancy shades the other methods appear destined to supplement this method. In piece dyeing, chrome mordanting always has the effect of cleaning wool pieces, thus favouring level results, but the indiscriminate use of strong chromium mordants on fine wools is to be deprecated as the wool becomes harsh by such a treatment.

Lime wool is a source of trouble by whichever method it is dyed, but dyers usually favour the chrome mordant method. When mordanting, it is advisable to mordant with bichromate and sufficient hydrochloric acid to remove all the lime as the

soluble calcium chloride. Sulphuric acid should never be used or insoluble calcium sulphate will be precipitated on the wool, thus making it harsh and sticky.

There are several methods of mordanting wool with sodium or potassium bichromate, using different assistants. In no case should the assistant be dissolved together with the bichromate or added to a strong solution of bichromate ; it should be dissolved separately and added to the mordanting bath just before the wool is entered. This precaution is necessary, since with bichromate and sulphuric acid so much free chromic acid would be produced before commencing to mordant that an unlevel result would be produced, whilst with bichromate and a reducing assistant like formic acid, chromic hydroxide would tend to be precipitated in the liquor instead of being gradually fixed on the wool during the mordanting process.

The following are the various mordants used and their application.

Bichromate Alone.—Bichromate alone (sweet chrome) is the mordant most commonly used in practice. In this method the wool is entered into a liquor at 50° C. containing 2–4 per cent. bichrome, the liquor raised to the boil in $\frac{3}{4}$ hour and boiling continued for 1–1$\frac{1}{2}$ hours. As the liquor is not exhausted a standing bath is often used which is replenished by adding the requisite small amount of sulphuric acid to re-convert the chromate left in the bath to bichromate and sufficient bichrome to replace that absorbed by the previous batch.

Bichromate and Sulphuric Acid.—Sometimes sulphuric acid (D.O.V.) is added to the mordanting bath in order to assist exhaustion, the amount used being one-third of the weight of bichromate, but unless the rate of mordanting is carefully controlled there is a tendency to produce uneven results. This method of mordanting is most frequently used when dyeing Logwood and Hematine, and is often used when mordanting shoddy, since some stripping of the ground colour on the shoddy also occurs simultaneously. The stripping effect with shoddy is frequently a more important requirement than the mordanting, which may be incidental and in such cases much higher quantities are used, as for example 6 per cent. bichromate and 12 per cent. sulphuric acid.

Bichromate and Tartar.—1–3 per cent. bichromate and $\frac{3}{4}$–$2\frac{1}{2}$ per cent. tartar (acid potassium tartrate) are used, the wool being entered into the mordanting liquor at 50° C., the liquor raised to the boil in $\frac{3}{4}$ hour and the wool boiled for 1–1$\frac{1}{2}$ hours. This method is more expensive than the above methods, but is frequently used for the better classes of work.

Bichrome and Oxalic Acid.—1–3 per cent. bichrome and 1–3 per cent. oxalic acid are used and applied as described under bichrome and tartar.

Bichrome and Formic Acid.—1–2 per cent. bichrome and 1–2 per cent. formic acid (85 per cent.) are used. Since the reduction of the bichrome with this assistant is very rapid, unlevel dyeings result unless the mordanting is carefully carried out. The wool should, therefore, be entered at 60° C., the liquor gradually raised to the boil, and boiling continued for 1–1$\frac{1}{2}$ hours. In this method the whole of the chrome in the bath is precipitated on the fibre so that less bichrome is used than in the other methods. Indeed the bath is so well exhausted of chrome that the same liquor may be used for dyeing as was used for mordanting.

Bichrome and Lactic Acid.—1$\frac{1}{2}$–3 per cent. bichrome, 3–5 per cent. lactic acid (50 per cent.) and 1 per cent. sulphuric acid (D.O.V.) are applied to wool as described under bichrome and formic acid. This method also gives excellent exhaustion of the mordanting bath.

Wool when mordanted with bichrome alone or with bichrome and sulphuric acid has a yellow colour due to the presence of chromic acid. These methods yield an oxidizing chrome mordant. With the other methods of mordanting the wool has a green colour due to the presence of chromic hydroxide on the fibre formed by reduction of the bichrome by the assistant; this is known as a reduced chrome mordant.

It is surprising what different results may be obtained from one and the same dyestuff by the use of bichromate with the above different assistants.

Hematine crystals are marketed in different states of oxidation and consequently give different results according to the mordant employed. Well-oxidized Hematine crystals will give a better result on a reduced than on an oxidizing mordant; conversely, partially oxidized Hematine crystals will give a better result on an

oxidizing than on a reduced mordant. Brilliant Alizarine Blue R (C.I. 931) gives the best result on a weak bichromate and oxalic acid mordant. Again, Gallocyanine gives shades fastest to rubbing on a bichromate and tartar mordant, whilst with bichromate and sulphuric, formic or oxalic acid the shade rubs badly. Solochrome Brown M (C.I. 104) also illustrates the influence of the assistant used. When dyeing heavy shades with this dyestuff on a chrome mordant, it must be dyed on a bichromate and acid mordant, and not on a bichromate and tartar mordant in order to get shades fastest to milling. All mordanted wool must be thoroughly washed before dyeing ; if this is not done the dyed shade is very liable to rub.

DYEING

The dyebath is filled with cold water and acetic acid or Calgon added, according to the hardness of the water used. Dyestuff pastes are mixed with acetic acid acidulated water to a thin uniform paste, which is then run into the dyebath through a fine sieve to prevent lumps getting into the dyeliquor, whilst powders (excepting the bisulphite compounds) are dissolved in boiling water before adding to the dyeliquor. The wool is entered into the cold dyeliquor and worked at a low temperature until most of the dyestuff is absorbed. When using the bisulphite compounds the temperature of the dyeliquor must not be raised above 65° C. until all the dyestuff has been absorbed, since above this temperature the bisulphite compound splits up and, unless it has been previously absorbed by the fibre, insoluble alizarine dyestuff is precipitated in the dyeliquor, thus wasting dyestuff and causing the dyeing to rub. The temperature is then gradually raised to the boil during $\frac{3}{4}$–1 hour and dyeing continued at the boil for 1–2 hours. If a very heavy shade is being dyed it is advisable to add $\frac{1}{2}$ per cent. bichrome to the dyebath when exhausted, and to boil for a further $\frac{1}{4}$ hour. This prevents any bleeding in subsequent milling, but as this after-chroming will have an effect on the shade, allowance must be made for this when matching to pattern.

If it is necessary to make a further addition of dyestuff in order to obtain the required shade, the temperature of the

dyebath is lowered by running off half the dyeliquor and filling up with cold water before making the addition.

Afterchrome Process.—This is a modification of what was formerly called the " saddening " process in the dyeing of the old dyewoods.   The most suitable dyestuffs for application by this method belong to the azo series and contain hydroxyl and carboxyl groups which give them their lake forming properties.   In general, the afterchrome process yields slightly faster results and gives less staining of effect threads than do the other methods ; it is widely used for heavy shades and particularly blacks, blues, and browns on loose wool, slubbing, yarn and pieces, but its adoption for light shades has proved slower owing to the difficulties of matching to pattern.   This difficulty arises owing to the fact that the shade cannot be judged until it has been developed with the bichromate.   As the difference in shade before and after the addition of the bichrome is often very marked a good deal of experience is, therefore, required to match accurately.   However, the difficulty of shading in a hot chrome liquor is not so great now that there are dyestuffs at the dyers' disposal quite suitable for this purpose.

If the amount of shading required is only slight, then acid milling dyestuffs may be used, but should the shade require a large addition of dyestuff, say $\frac{1}{2}$ per cent. or more, then chrome dyestuffs should be used.   When shading the steam is shut off, the well-dissolved dyestuff added, the steam put on again and boiling continued $\frac{1}{4}$ hour.

The great advantage of this process is that it is a shorter one than the chrome mordant method and is therefore economical in time, labour, and steam, whilst the wool is left in better condition.   Dyeings of excellent fastness are obtained, which are faster than dyeings of the same dyestuffs applied on a chrome mordant.   This method is largely used, and is most suitable for dyeing loose wool (especially for big lots of one shade, such as Khaki) since if one batch comes off shade, another lot may be dyed to counterbalance it to carry it through the blending.   For yarns and pieces there is not the same latitude in matching as there is with loose wool, which is why its use is confined mainly to darker shades, but the method is now being adopted for all types of shades excepting very light ones.

The dyeing is carried out as follows : The dyestuff is boiled along with 10 per cent. Glauber's salt in about a foot of water at the bottom of the dye-vessel ; when the dyestuff has dissolved the bath is run up with cold water, 1–5 per cent. acetic acid is added, and the liquor well stirred. The material is entered at 50° C., the dyeliquor gradually raised to the boil in $\frac{1}{2}$ hour, and dyeing continued at the boil for $\frac{1}{2}$ hour. If the dyeliquor is not exhausted, $\frac{1}{2}$–2 per cent. sulphuric [D.O.V.] or formic acid is added and boiling continued $\frac{1}{4}$–$\frac{1}{2}$ hour longer until exhaustion is obtained. When the bath is exhausted—and not before, or the dyeing will not be fast to milling—1–2 per cent. bichrome is added, and boiling continued $\frac{1}{2}$ hour. It has proved advisable in practice when dyeing wool, which has subsequently to be heavily milled with rayon or mercerized cotton—to continue boiling in the chrome up to $\frac{3}{4}$–1 hour. The effect of this additional boiling is very beneficial in preventing subsequent staining of the rayon or cotton. Clearer effects are obtained by washing off, followed by chroming in a separate bath. After dyeing to avoid shade changes due to the prolonged action of the hot acid chrome liquor and to maintain the spinning qualities of the wool no delay should take place before the wool is washed off.

Fast Chrome Blacks.—These blacks are universally employed in the dyeing of all forms of wool, so that they have received a large amount of attention at the hands of the dyestuff manufacturer. The first members of this class of dyestuffs were not fast to potting ; a process for giving wool cloth a special finish which consists in wrapping the cloth round a roller and immersing it in water at various temperatures for 24 hours. As many as six repetitions of this process may be necessary before the requisite finish is obtained. The introduction of the dry-blowing of pieces has lessened the severity of the process.

It is essential that the dyestuff used does not bleed into adjacent white or coloured threads. At one time the only blacks which would withstand this process were Logwood Black (C.I. 1253) and Alizarine Black ; earlier chrome blacks, like Diamond Black F (C.I. 299) would not.

In recent years there has been introduced a large range of what are termed potting blacks, of which the first was Diamond Black

PV (C.I. 170). These frequently have the prefix " P " attached to them as an indication that they are fast to potting, but their merits in this respect vary considerably. They are quite distinct from the non-potting variety in that they are more soluble, will stand much more sulphuric acid in the dyeing, and require more bichromate to develop the correct shade. These very properties have made them an ideal black for the dyeing of carbonized rags. If carbonized rags are dyed with the Diamond Black F class the acid in the rags exhausts the dyeliquor so quickly that the dye-stuff is only dyed on the surface of the rags, with the result that when they are subsequently pulled up they appear grey, due to lack of penetration. The " PV " class, owing to their greater solubility and less sensitivity to acids, do not dye on so quickly, and therefore give better penetration. For this reason they have become of the highest importance in the rag-dyeing trade. As a rule the potting blacks are not of the same fastness to light as the non-potting blacks. Diadem Chrome Black PV is not as fast as Diadem Chrome Black F, but like every rule, it has its exceptions, in this case with Eriochrome Black T (C.I. 203) and PB conc. which possess excellent fastness to light. Whilst both classes of blacks possess excellent fastness to milling, the " P " brands are the faster in that they leave rayon and mercerized cotton used for piece dyeing effects cleaner in the heaviest milling—these being most difficult to keep untinted in milling.

Fast chrome blacks, when dyed as detailed below, possess excellent fastness to milling, light, acids, and alkalies, and are quite suitable for machine dyeing. The method of dyeing is as follows : The dyebath is prepared with the requisite amount of dyestuff, 10 per cent. Glauber's salt and 5 per cent. acetic acid, the wool entered into the hot dyeliquor, the temperature raised to the boil, and boiling continued for $\frac{1}{2}$ hour. $\frac{1}{2}$–2 per cent. sulphuric [D.O.V.] or formic acid is then added, boiling continued for 20–30 minutes, when the dyestuff should be exhausted, 1–2 per cent. bichrome added and boiled for $\frac{1}{2}$ hour. In no case must the bichrome be added until the dyestuff is exhausted, or a brown shade black will be the result. Within certain limits, the shade of the fast chrome blacks may be controlled by the amount of sulphuric acid and bichrome which is used ; thus, $\frac{1}{2}$ per cent. acid and 1· per cent. bichrome will give a much bluer shade than

2 per cent. acid and 2 per cent. bichrome, which will yield a dead black.

If the black has to be subsequently heavily milled with rayon or mercerized cotton it is advisable to boil $\frac{3}{4}$–1 hour in the bichrome, because this has a beneficial effect in preventing bleeding. The two places in which it is possible to go wrong when dyeing chrome blacks are as follows : the sulphuric or formic acid must not be added till the bath has boiled at least $\frac{1}{2}$ hour, or the dye-stuff will be dyed on too quickly, so that proper penetration will not be obtained, probably coupled with uneven results ; the bichrome must not be added till the dyebath is exhausted, or a poor shade of black tending to brown, which rubs, will be obtained.

Potting chrome blacks are dyed as above, except that 2–3 per cent. sulphuric or formic acid must be added to exhaust the dyestuff instead of $\frac{1}{2}$–1 per cent. and 2–3 per cent. bichrome must be added in order to obtain complete development of the black.

The chrome blacks before chroming are usually dull claret shades, which are converted to black on boiling with the bichrome. These blacks do not give satisfactory shades on chrome mordant, and are practically never applied by this method. Eriochrome Black A is an exception and gives good results on chrome mordant. They cannot be dyed by the metachrome method.

True alizarine dyestuffs are never applied by the after-chrome method, with the possible exception of Alizarine Red S powder, which is sulphonated and, therefore, is soluble.

Chromotrope Dyestuffs.—These are easy levelling red acid dyestuffs, which may be used as acid reds of quite good fastness to light, but which on chroming are turned into blue shades of great fastness to light. They are largely used for the dyeing of navy blues on piece goods, and have become standardized for certain classes of dress goods. Many of the dyestuffs so used are combinations of various bases with chromotrope acid (di-oxy naphthalene-di-sulphonic acid 1 : 8 : 3 : 6) from which their name is derived.

They are dyed like ordinary acid dyestuffs with Glauber's salt and acetic acid, and exhausted with sulphuric or formic acid, but after $\frac{1}{2}$–1 hour's boiling 2–3 per cent. bichromate, 1–3 per cent. lactic acid and 1 per cent. D.O.V. are added and boiling is

continued ½–1 hour.   The shade gradually changes from red to navy blue as the chroming proceeds, so that a large range of blues may be obtained, according to the length of time of boiling in the chrome liquor.   The longer the wool is boiled with the bichromate the greener does the shade develop ; the addition of more bichromate has a similar effect.   Since many of the navy blues so obtained are on the red side, it is common practice to add a little acid green to correct this redness.   Lactic acid has the specific property of assisting development or greening of the shade in chroming and in this respect cannot be replaced by formic or any other acid.   Too much acid tends to delay the full development of-the shade ; copper salts act similarly.   The weakness of this group is that the shades obtained by this method frequently turn red in artificial light, so that shading with a little bright blue or green acid dyestuff turning green in artificial light has the further advantage of correcting this redness in artificial light. It should also be noted that the chromotropes do not possess the same wet fastness properties as ordinary afterchrome dyestuffs and are, therefore, not suitable for application to loose wool, slubbing, etc., which have subsequently to be milled.   Unless completely developed a pink bleeding due to undeveloped dyestuff is liable to take place in subsequent wet processing ; complete development is difficult to achieve.

Metachrome Process.—This modification of the after-chroming process was originated by the Berlin Aniline Co.'s patent of 1900 dealing with a special mordant, known as Metachrome mordant consisting of a mixture of potassium chromate and ammonium sulphate.   Nowadays, dyers usually make their own metachrome mordant from bichromate, which is made alkaline with ammonia so as to convert it to chromate and then adding to the chromate solution ammonium sulphate which has also been made alkaline with ammonia.

If bichromate is added to a dyebath containing certain mordant dyestuffs immediate precipitation of the dyestuff as the chromium lake takes place, whereas if the bichromate is converted into chromate by the addition of ammonia there is no precipitation, and the dyestuff lake is then only precipitated if the dyebath subsequently becomes acid.· The ammonium salt provides a source from which acid may be slowly liberated as dyeing pro-

ceeds and thereby reconvert the chromate to bichromate which fixes the dyestuff. It has been commonly believed that ammonium salts when used in wool dyeing dissociate into ammonia and the corresponding free acid, and that as boiling proceeds the ammonia volatilizes and the dyebath becomes more acid.

Briggs and Goodall (*J.S.D.C.*, 1939, p. 354) have shown that in concentrations similar to those used in practical dyeing the development of acid is very small and the main effect of the presence of ammonium salts in dyebaths is to neutralize any alkalinity present in the scoured material to be dyed. Volatilization of ammonia on boiling in absence of wool is appreciable, though not great, and increases in the order chloride, sulphate, formate, oxalate and acetate, *i.e.* it is a function of the dissociation constant of the acid from which the salt is derived. In the presence of wool the ammonia volatilized from ammonium chloride and sulphate is increased four-fold, but from the ammonium salt of the organic acids there was no significant difference. This is stated to be due to the fact that the mineral acids liberated are almost entirely sorbed by the wool, whereas the organic acids remain in solution. See also Goodall and Hullah (*J.S.D.C.*, 1940, p. 218) ; Goodall and Hobday (*J.S.D.C.*, 1940, p. 384).

As originally introduced, the metachrome process was confined to a comparatively small number of dyestuffs derived from picramic acid $NH_2(NO_2)_2C_6H_2OH$, but there is now available a large range of suitable dyestuffs. Many dyestuffs, true Alizarines and the Gallocyanines, are precipitated even by the chromate and so may not be applied by this method. This process, which is alternatively known as monochrome, chromate and autochrome method has one distinct advantage over the other two methods already described. As compared with the chrome mordant method it is a single as against a two-bath process, which is a great economy in time, labour, water, and steam, thus giving increased output. Again, compared with the top-chroming method there is a considerable saving in time, and development of shade begins as soon as the dyeliquor is boiling, so that the dyer is sooner able to see how the final shade is developing. It has, therefore, achieved great popularity in loose wool, slubbing, yarn, and piece dyeing, especially for the production of pale and medium shades, but many heavy shades cannot be dyed

satisfactorily by this method since only poor colour value is obtained.

The method of dyeing is as follows : the dyestuff is boiled in a foot of water in the bottom of the cistern until completely dissolved, the cistern is filled up with water. The requisite amount of bichromate and ammonium sulphate are added to the dye-liquor immediately before the wool is entered. Loose wool or slubbing is entered into the boiling dyebath, but in the case of yarn it is advisable to enter not higher than $60°$ C. Dyeing is continued for $\frac{3}{4}-1\frac{1}{2}$ hours at the boil, when the shade should be fully developed.

In the authors' opinion ammonium sulphate gives the best results, but it may be replaced by acetic acid. If acetic acid is used, it must not be added till the bath has boiled half an hour, and then it must be strongly diluted. Some dyers use formic or sulphuric acid [D.O.V.], but their use is to be deprecated, because they do more harm than good unless they are added very skilfully. The average amount of bichromate required is half the total weight of the dyestuff used up to a maximum of 3 per cent. bichromate, but the proper amount is always given by the respective dyestuff makers. For every pound of bichromate used $2\frac{1}{2}$ lb. ammonium sulphate, $2\frac{1}{2}$ lb. acetic acid, or 1 lb. formic acid or sulphuric acid is added. The minimum quantity of bichromate which should be used is 1 per cent. of the weight of wool, because it must always be remembered that the wool itself absorbs a certain quantity. Other dyestuffs than mordant dyestuffs may be used by this process, providing the dyestuff withstands the action of the bichromate and it is fast to milling and light.

When dyeing skin wool, *i.e.* wool which has been removed from the pelt by lime, and is therefore full of lime, it must be noted that the shade takes longer to develop since the development is retarded by the alkalinity of the lime. More acid may, therefore, be needed.

This process is particularly suitable for machine dyeing and requires no special precautions except that it is advisable not to add the bichromate until the dye-liquor has been circulated a quarter of an hour at the boil. This precaution ensures the material being thoroughly saturated with the dyestuff before the bichromate commences fixing it on the fibre.

For shading purposes acid dyestuffs fast to milling may be used, such as Polar Brilliant Blue or mordant dyestuffs which are not precipitated by bichromate or acid. Where yarn is being brought to shade with such mordant dyestuffs it may be advisable to add a little ammonia to the bath before re-introducing the yarn, but with loose wool this will not often be necessary. Steam is, of course, shut off whilst the perfectly dissolved dyestuff is added.

Correction of Uneven Shades.—Owing to the fastness of the mordant dyestuffs it naturally follows that they are very difficult to correct. One of the best methods of achieving this is to boil the wool with fairly strong sulphuric, hydrochloric, or oxalic acid, which has the effect of splitting up the chrome-dyestuff lake. This is followed by a warm ammonia bath to remove the dyestuff which has been split from the chrome-dyestuff complex by the acid treatment.

Silk.—The true alizarine dyestuffs on chrome and alum mordants are used very extensively on silk yarns, but seldom on piece goods, yielding shades of excellent fastness to light, washing and boiling soap, which are not much inferior to those obtained with vat dyestuffs. In order to preserve its lustre the silk is not mordanted in the same way as wool, and many methods have been suggested for this purpose. Mordanting with alum is carried out by soaking the silk for about 12 hours in cold basic aluminium sulphate (prepared by dissolving 3 lb. aluminium sulphate in 10 gallons of water and adding 2 lb. of soda ash previously dissolved in water), wringing, and fixing with cold 1° Tw. sodium silicate for $\frac{1}{2}$ hour. Mordanting with chrome is carried out on similar lines using 32° Tw. chromium chloride or 9° Tw. chrome alum and fixing with $\frac{3}{4}$° Tw. sodium silicate. By this means basic chromium salts are precipitated on the fibre. According to a recent method (Hishiyama and Sehiguchi, *J.S.C.I. Japan*, 1932, pp. 35, 113b ; *J.S.D.C.*, 1932, pp. 181, 316) the silk is boiled with 20–40 per cent. chrome alum for 30 minutes, and then dyed without drying. Dyeing is carried out in a soap or boiled-off liquor bath broken with acetic acid. The silk is entered into the cold dyebath, the temperature raised to the boil in $\frac{3}{4}$ hour, and dyeing continued at a gentle boil for 1 hour. Handle and lustre are improved by an after-treatment with boiling soap. A large

number of the true alizarine and other mordant dyestuffs may be dyed in this way, but as the fastness of the shades obtained by this method varies with mordant dyestuffs other than the true alizarine series, preliminary tests should always be made of such dyestuffs before adopting them on the large scale.

In the dyeing of silk noils where the preservation of the lustre is not of equal importance the after-chroming and metachrome methods may be used with advantage. For details see under " Wool."

Cotton.—The main use of the true alizarine dyestuffs on cotton is the dyeing of Alizarine on a calcium-aluminium-mordant to produce the well-known Turkey Red, but in calico printing their application is much more widespread (see Knecht and Fothergill, " The Principles and Practice of Textile Printing," 1936).

Turkey Red dyeing on cotton is a section of the dyeing trade which has become concentrated in the hands of a few firms in the countries in which it is dyed, and the authors make no claim to any experience in this special line of dyeing. It is one of the oldest processes extant and travelled from the East Indies to France *via* Persia, Armenia, Syria to Turkey, and Greece. 1790 is given as the probable date of its introduction into Great Britain and the Vale of Leven was the locality in which it was most largely dyed. The process as carried out in the olden days lasted as long as 4 months, but has now been cut down to three days, though the fastness is not as good. The distinction between these two processes is that in the old process the oil used is rancid olive oil, whilst in the new process the oil used is sulphated castor oil. Repeated washing tests show that the old process gives the faster dyeings, but it must not be thought that the new Turkey Red is not a satisfactory dyestuff, because it also gives very fast dyeings.

Turkey Red as produced on the fibre is not a simple aluminium alizarine lake, but according to Fierz-David and Rutishauser (*Helv. Chem. Acta.* 1940, p. 1,289) is a hydrated complex containing alizarine, aluminium and calcium in the proportion 4 : 2 : 3. These authors state that the fatty materials used in Turkey Red dyeing probably serve first to fix the metal oxides on the fibre in the form of soaps and then to bring the lake into the finest

dispersion. Later they separate out from the complex which then only consist of alizarine, oxides of aluminium and calcium and water. The calcium in the lake can be replaced by other divalent metals without appreciably altering the colour which appears to be determined by the trivalent metal present.

The importance of Turkey Red on cotton has been considerably minimized due to the development of the wide range of azoic dyestuffs which enable dyeings of satisfactory fastness to be obtained by simpler methods (see Section X.).

Section VIII.—DIRECT COTTON DYESTUFFS.

The Direct Cotton dyestuffs include the following chemical groups, which are all applied by the same method of dyeing.

Disazo dyestuffs .. .. Benzopurpurine 4B (C.I. 448).
Trisazo dyestuffs .. .. Chlorazol Black FFS (C.I. 539).
Tetrakisazo dyestuffs .. .. Toluylene Brown R (C.I. 609).
Stilbene dyestuffs .. .. Stilbene Yellow (C.I. 622).
Thiazol dyestuffs .. .. Primuline (C.I. 812).
Dioxazine dyestuffs .. .. Sirius Supra Blue FFRL.

The first member of this class to be marketed was Congo Red (C.I. 370) discovered in 1884 by Böttiger (E.P. 4415). Though its fastness, particularly to acids, left much to be desired it met with a ready sale until it was supplanted by its higher homologue Benzopurpurine 4B. As Congo Red dyed cellulosic fibres without previous mordanting its influence on dyeing practice was epoch-making, since most of the then known dyestuffs could only be applied to mordanted cellulosic fibres. The importance of this dyestuff was immediately appreciated by the dyestuff manu-facturers, who displayed intense activity in the search for other examples, with the result that a large range is now available (see Rowe, "Colour Index," 1924). Their simple method of appli-cation was welcomed by dyers, and made possible an enormous extension in the dyeing of mixed fabrics of silk, wool, cotton, and rayons, whilst the success of present-day garment dyeing is also largely attributable to these dyestuffs. Like all groups of dye-stuffs, the individual members possess widely divergent properties. Thus the group includes Congo Red which is so sensitive to acids that it is used as a mineral acid indicator, and Chlorazol Fast Scarlet 4BS (C.I. 327) which is so fast to acids that it will with-stand treatment with strong nitric acid. Again, it includes a dyestuff as fugitive to light as Primuline, and one as exceptionally fast to light as Solophenyl Red Brown. The temperature at which direct cotton dyestuffs dye to a maximum depth also

varies considerably with the individual dyestuffs, *e.g.* Chryso: phenine G (C.I. 365) will dye cotton almost as full a shade at 40° C. as it does at the boil, whereas Chlorazol Fast Scarlet 4BS does not appreciably dye the cotton below 60° C. Many examples of the individuality of the direct cotton dyestuffs are detailed in the Rayon section (XIII.), and the remarks therein apply with equal force to the dyeing of mercerized cotton and to a less extent to ordinary cotton dyeing.

It may rightly be claimed that progress in this group of dyestuffs has been continuous by the constant introduction of dyestuffs of improved fastness, so that there are now available direct cotton dyestuffs of very good fastness to light, washing, etc. Although considerable progress has been made in this direction there is still scope for yet further improvements as the following examples will show. There was no blue, grey, or black which had a fastness to light equal to that of Chlorazol Fast Orange AG or Solophenyl Red Brown, so that when a mixture of these two dyestuffs was shaded with flattening agents and exposed to light an unbalanced fade resulted due to the more rapid fading of the dyestuff used for flattening. This gap was partly filled by the introduction of such dyestuffs as Sirius Supra Grey VGL which is equally as fast as the fastest oranges and reds, also Sirius Supra Olive GL, which although not as fast to light, is a considerable improvement on the dyestuffs previously available. Again, a red is still required, which is as fast as Solar Orange RGL, or Diphenyl Fast Blue Green BL when given a soaping to remove surplus dyestuff immediately following dyeing.

MECHANISM OF DYEING

For many years numerous researches have been made on the theory of the dyeing of cellulose with direct cotton dyestuffs and very diverse mechanisms have been suggested often on insecure experimental foundations. A detailed account of this earlier work is beyond the scope of this book and the interested reader is referred to a summary of the literature by Valkó (" Kolloidchemische Grundlagen der Textilveredlung," 1937). The more recent publications on this subject have been reviewed

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by Boulton and Morton (*J.S.D.C.*, 1940, p. 145) who put forward what may be termed " the molecular theory of the dyeing of cellulose " which is summarized below.   In order to understand this theory clearly, it is necessary to have some knowledge of the state of the dyestuff in solution, the structure of cellulose, and of the method of transference of dyestuff from the solution to the fibre and its subsequent fixation in the interior of the fibre.

The direct cotton dyestuffs in solution are considered to be composed of particles of all sizes from single molecules up to large miscelles which are present together in a state of dynamic equili-brium.   The aggregation of these dyestuffs is probably explained by the formation of co-ordinate bonds between the aggregating molecules, *e.g.* hydrogen bonds between such polar groups as hydroxyl, amino, etc.   As the dyestuff molecules are absorbed by cellulose they are replaced (in a few seconds at 90° C.) by similar particles in sufficient quantity to restore the disturbed equilibrium.

At the present time there are several views on the structure of cellulose (see p. 13) but for this theory of dyeing it is sufficient to consider cellulose as composed of a three dimensional network of chain molecules lying approximately parallel to each other with here and there regions in which the arrangement of the chains attain crystalline regularity, *i.e.* there are amorphous and crystalline regions existing side by side.   When cellulose is im-mersed in water it is swollen and osmotic forces tend to cause the chains to move apart, but in the crystalline regions this is prevented by crystal forces, as is shown by the similarity in the X-ray dia-grams of wet and dry cellulose.   Between the crystallites in the swollen condition the molecular chains will form an open network through which small molecules may pass with ease.

Absorption of dyestuff from aqueous solution by cellulose is best conceived as an equilibrium between the tendency of the dyestuff molecules to be absorbed and the opposite tendency to dissolve in the water phase.   The affinity of the dyestuff for the water phase can be reduced by the addition of salt which, therefore, favours an equilibrium displaced to give an increased amount of dyestuff on the fibre.   In this connection it is interesting to note that Hanson, Neale, and Stringfellow (*Trans. Faraday Soc.*, 1935 p. 1718) have shown that pure direct cotton dyestuffs are not

PLATE 9
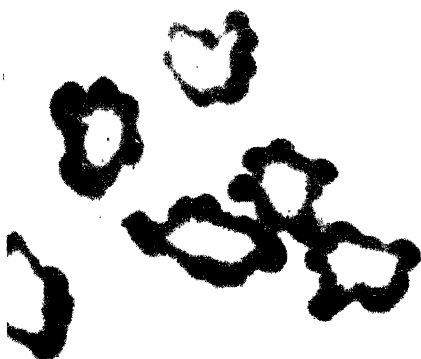
500/57 viscose rayon yarn dyed with 1 per cent. pure Benzopurpurine 4B (40 volumes) for *5 minutes* at 90° C. ×400.
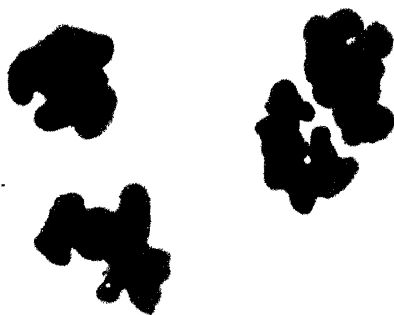
500/57 viscose rayon yarn dyed with 1 per cent. pure Benzopurpurine 4B (40 volumes) for *24 hours* at 90° C. ×400.

absorbed by cellulose in the absence of salt, and that absorption is capable of a quantitative explanation in terms of an ionic equilibrium of the Donnan membrane type. The rate at which equilibrium is attained depends on the dyestuff used and is increased by raising the temperature of the dyeliquor.

It appears likely that the union of dyestuff and cellulose is a co-ordinate bond (hydrogen bond) between the polar amino, hydroxyl, etc., groups of the dyestuff molecule and the hydroxyl groups of the cellulose. As the majority of direct cotton dye-stuffs, such as Benzidine dyestuffs, possess a thin elongated molecule it is probable that they lie with their long axis parallel to the axis of the long cellulose molecular chain on which they are fixed. This is in agreement with the dichroic behaviour of dyed cellulosic fibres (see Preston, *J.S.D.C.*, 1931, p. 312). Thus ramie fibre dyed with Congo Red is colourless when observed in polarized light with its length parallel to the plane of polarization, and deeply coloured when its length is perpendicular to the plane of polarization. The dyestuff molecules must, therefore, like the cellulosic molecular chains, be oriented with their long axes parallel.

When a cellulosic fibre is dyed to equilibrium the dyestuff is uniformly distributed throughout the fibre and is not confined to the superficial layer. This is illustrated by the photomicrographs of viscose [see Plates (supplied by Morton and Boulton)]. After 5 minutes' dyeing it will be noticed that the dyeing is mainly confined to the surface of the filaments but that after 24 hours the filaments are uniformly dyed. It will thus be seen that the dyestuff diffuses into the cellulose as dyeing proceeds until equilibrium is obtained.

From the above considerations it is postulated that when a cellulose fibre is immersed in a solution of a direct cotton dyestuff containing salt, dye molecules are immediately absorbed by the cellulose chain molecules forming the surface of the fibre. The dyestuff molecules then pass by a process of diffusion into the interior of the fibre by the capillary pores between the inter-crystalline regions of the swollen cellulose structure. The dye-stuff solution is thus depleted of its single molecules due to their absorption by the cellulose. These are, however, continuously replaced by the partial and gradual breakdown of the larger

aggregates into single molecules, until final equilibrium between the cellulose and dyestuff solution is reached. With some direct cotton dyestuffs the time taken to attain equilibrium is so long that it is never reached in commercial practice (see Section XIII.).

APPLICATION

Dissolving.—Although most of the direct cotton dyestuffs are readily soluble in water the dyestuff should be stirred into a smooth paste with cold water and whilst stirring boiling soft water poured on to the paste. This precaution prevents the dyestuff from forming gummy lumps or floating on the surface of the water, which may occur if boiling water is poured directly on to the dry dyestuff. The authors are aware that this method is not always followed in practice, but nevertheless the above method is the surest and safest way to avoid bad results due to fleckiness of the material caused by particles of undissolved dyestuff.

For the convenience of dyehouse routine many of the dyestuffs which are in constant use are kept in stock solutions. The additions of dyestuff to the dyebath for shading purposes are usually very small, so that solutions of the dyestuff used enable the dyer to measure out accurately and quickly the requisite amount of dyestuff to be added.

Assistants Used.—Since the direct cotton dyestuffs when used alone do not dye to exhaustion, an assistant is usually required to increase the affinity of the dyestuff for the fibre. The three assistants used for this purpose are Glauber's salt, sodium sulphate, and common salt ; 12 parts of Glauber's salt=6 parts of sodium sulphate (dessicated Glauber's salt)=5 parts of common salt. If the water used in dyeing is hard and a soft finish is desired Glauber's salt or sodium sulphate should be avoided, as the calcium sulphate formed on its addition would make the finished dyeing harsh. Alternatively, Calgon sufficient to overcome the hardness of the water, should be added to the water before adding the assistant. In countries like France and Italy, where common salt is subject to a revenue tax, its cost prohibits its use in dyeing and desiccated Glauber's salt is used.

The average amounts of assistant required for dyeing the

direct cotton dyestuffs in a liquor ratio of 30 : 1 are indicated below :—

0·1 per cent. dyestuff ..		..	..	5	per cent. common salt.	
0·5 ,,	,,	..	.. 7·5	,,	,,	
1·0 ,,	,,	..	.. 10	,,	,,	
2·0 ,,	,,	..	.. 20	,,	,,	
3·0 ,,	,,	..	.. 30	,,	,,	
4·0 ,,	,,	..	.. 40	,,	,,	

In lower liquor ratios, such as are used in pack dyeing, correspondingly less amounts of assistant are necessary. It should also be noted that the salt sensitivity of individual direct cotton dyestuffs varies widely, which is another factor in determining the amount of assistant to be used.

Soda ash has been widely recommended as an addition to dyebaths of direct cotton dyestuffs to increase the solubility of the dyestuff, the object being to decrease the rate of absorption and thus ensure better penetration of the dyestuff into the fibre's structure. More recent work (Whittaker, *J.S.D.C.*, 1936, p. 68) has, however, shown that the addition of soda ash to a dyebath for this purpose is a fallacy, as the soda ash does not retard dyeing, but actually acts as a salting agent. This can readily be shown by dyeing Benzopurpurine 4B or Chlorazol Fast Orange AG at 90° C. on either cotton or viscose, without the addition of Glauber's salt or common salt (liquor ratio 40 : 1) but with and without an addition of 5 per cent soda ash, when it will be found that the dyeing made in the presence of soda ash is much heavier than the dyeing made without this addition. This effect is still more marked when dyeing in a lower liquor to material ratio, and when using concentrated dyestuffs.

Soap, monopole oil, soluble oil and many of the new auxiliary products, *e.g.* Lissapol LS, Sapamine FL, etc., are frequently used. These substances in yarn dyeing facilitate the opening of the skeins in roller machine dyeing, whilst they also give a soft handle to the finished goods. As was the case with soda ash it has been frequently stated that the soap, etc., retards the dyeing of direct cotton dyestuffs, but subsequent work (*ibid.*) has shown that soap also acts as a salting agent with salt-sensitive dyestuffs such as Benzopurpurine 4B. This fact, that soap acts as a salting

agent in some circumstances, was first observed by the authors during the dyeing of viscose rayon skeins by a foam-dyeing method.

Acetic acid has a very limited use with the direct cotton dye-stuffs, being chiefly used when dyeing bright blues of the Isamine Blue (C.I. 710) and Direct Sky Blue type (C.I. 518).

DYEING

Cotton.—Cotton may require to be dyed with direct cotton dyestuffs in one of the following forms :

1. Loose cotton, sliver, roving.
2. Yarn, including cops, cheeses, hanks, warps, and beams.
3. Piece.

In principle, the application of these dyestuffs is simplicity itself in that dyeing is done at the boil until the material is dyed to the required shade. In actual practice, however, there are several factors, demanding the experience and judgment of the foreman dyer, which have to be taken into consideration. Some of these are indicated below.

As already indicated (p. 6) different direct cotton dyestuffs dye at very widely different rates, a behaviour which may cause considerable trouble when dyeing compound shades, unless dyestuffs dyeing at the same rate are chosen. Again, dyestuffs which dye slowly at the boil should be used where penetration and evenness are of the greatest importance. For jig dyeing, dyestuffs giving maximum colour value at 60°–70° C. are best, whilst for padding purposes dyestuffs of excellent solubility, which dye rapidly to give full shades at low temperatures give the most satisfactory results. In package dyeing use should only be made of dyestuffs which are easily soluble and possess good penetrating powers due to slow rate of exhaustion, so that the goods are probably penetrated ; also, only those dyestuffs should be used which are sufficiently pure to retain their shade and solubility in a standing bath. The use of concentrated dyestuff types will be found to be particularly suitable for use in package dyeing. For shading purposes, dyestuffs which exhaust slowly should be chosen. For example, it would be courting disaster to add a small quantity of Chlorazol Brown M to a boiling dyebath

because it would dye on too quickly and, therefore, unevenly, whereas Chlorazol Drab RH could be used with safety under the same circumstances, as this dyestuff does not rush on to the fibre.

As the direct cotton dyestuffs vary widely in their rate of exhaustion a considerable amount of dyestuff may be left in the dyebath. This can be minimized by keeping the volume of liquor as low as possible, but the volume should not be reduced too low because the cost of dyestuff so saved is negligible compared with the cost of correcting a batch of goods spoilt through not having sufficient liquor in which to work them adequately. In open cistern dyeing 30 times liquor calculated on the weight of cotton is the minimum quantity in which loose cotton may be efficiently dyed if the cotton has to be poled (stirred) by hand ; for yarn 20–25 times liquor calculated on the weight of cotton is the average amount used in the ordinary yarn beck or on the Gerber and Hussong types of machine ; for piece dyeing, jiggers are used in which the amount of liquor used will not be more than 6 times the weight of the cotton. The amount of liquor used may be as low as 5 times the weight of the cotton with most of the pack dyeing machines which are finding increasing use for dyeing loose cotton, sliver, roving, cops, cheeses, hanks, warps, and beams.

On the face of it, it may appear economical to retain the dye-liquor which has not been exhausted, but in practice this is not always feasible, as, with the exception of shades for which there is a constant demand, such as blacks, navies, and reds, it is not often possible to maintain the dyeliquors due to lack of storage cisterns. Where machines are used, however, it is easier to reserve several liquors by having several storage tanks suitably interconnected. Old dyeliquors should be replenished, for example, with three-quarters of the original amount of dyestuff taken and one-quarter of the original amount of assistants. Care should be taken to avoid too much common salt in the dyebath which would precipitate the dyestuff, and the cold dyeliquor should, therefore, not stand at more than 6°–8° Tw. when dyeing dark shades. Cotton dyed in the loose form always requires the most weight of dyestuffs to obtain a specific shade, whilst cotton pieces require the least, mainly due to the differences in penetration obtained by dyeing in these two forms.

When a shade comes out darker than the desired shade, or if the dyeing is uneven, it may be sufficiently stripped for correction in many cases by boiling in a clean bath with soap and carefully salting back the dyestuff removed by the soaping. If this treatment is not effective the shade may be stripped with alkaline hydrosulphite or by a mild treatment with cold dilute sodium hypochlorite, and re-dyed.

Loose Cotton.—Formerly loose cotton was dyed with direct cotton dyestuffs in large wooden vats or iron pans, the dry cotton being thrown into the boiling dyeliquor and the material moved through the dyeliquor by poleing. As this method requires much labour, and gives unlevel results, together with a small production, dyeing is now mostly carried out in one of the many forms of circulating or pack machines which are capable of dyeing upwards of 1,000 lb. of loose cotton at a time. In such machines the loose cotton should not be too tightly packed or free circulation of the dyeliquor which is necessary for good penetration will be prevented. Loose cotton dyed by the pack method will obviously be a better spinning proposition than that dyed in open cisterns and poled by hand.

The cotton is either first boiled out or a wetting agent added to the dyebath. Dyeing is started at the boil; after 15 minutes dyeing salt is added, and dyeing continued at the boil for 1 hour or more. For heavy shades, the steam may be shut off after dyeing for $\frac{1}{2}$-hour, and the cotton allowed to feed in the cooling dyeliquor.

Providing the loose material has been carefully handled and no matting has taken place the fibre can be satisfactorily spun. Cotton dyed in the loose form and then spun into yarn will process and weave more satisfactorily than hank dyed yarns and will give less waste. In addition, perfectly level well-penetrated shades are obtained since any unevenness in dyeing is eliminated by the mixing of the fibres during the carding operation. Dyeing in this form can, however, only be done economically if large weights are to be dyed to the same shade, since when changing the shade on the carding engine the cards need to be thoroughly cleaned, thus losing both time and production.

Cotton Hanks.—Cotton is dyed with direct cotton dyestuffs in hank form for the production of pattern warps and for use as

weft ; an alternative method being to dye it in cop or cheese form.

Before dyeing, cotton hanks are usually wetted out or boiled out, whilst if light shades are to be dyed preliminary bleaching is often necessary (see p. 52). Wetting out is usually sufficient for condenser yarns which have to be dyed in medium or heavy shades, but experience has shown that fine yarns are preferably kier boiled (see p. 50). It must be realized that wetting out methods do not remove cotton seeds, which can only be satisfactorily removed by pressure kier boiling.

In dyeing, the yarn is usually entered at 60° C. given a couple of turns, the bath then brought to the boil, and dyeing continued at the boil for $\frac{1}{2}$–$\frac{3}{4}$ hour. When dyeing dark shades the yarn may be entered direct into the boiling bath and after three-quarters of an hour's boiling, steam is shut off, and the yarn allowed to feed in the cooling bath. If difficulty is experienced in getting any shade even, the salting-on assistants should be added in several portions only after the yarn has been boiled in the dyeliquor for a quarter of an hour.

The dyeing of cotton hanks on yarn dyeing machines of the roller type is carried out as described above. With these machines the essential but expensive labour of turning the hanks by hand is replaced by the machine, and batches up to 500–600 lb. of yarn can be entered all at once into the dyeliquor and turned simultaneously, which cannot be done when dyeing by hand. Moreover, one man may also supervise more than one shade at the same time when the machine is suitably divided into several sections. Cotton yarns are also dyed in the various forms of pack dyeing machines (see p. 74).

Cotton Warps.—The direct cotton dyestuffs are very largely used in dyeing shades on warps to be woven into flannelettes, shirtings, pyjamas, zephyrs, etc. If necessary, the warps are first boiled out in a four-box warp machine, or they may be plaited into a kier and pressure boiled. The warps should, whenever possible, be doubled up so as to make the run as short as possible, and to minimize the possibility of ending by incorrect feeding of the dyeliquor. The dyeing process is similar to that for cotton hanks, but owing to the shorter time of dyeing the dyeliquor must be much more concentrated, and the resulting

dyeings are not as well penetrated as hank-dyed yarn. For dyeing pale shades one box of the machine may be sufficient, whereas for dark shades and blacks three boxes may be used in order to obtain the depth of shade required in 1–2 runs. Sky blues, pinks, creams, etc., may all be dyed at one end, providing the labourer in charge of the machine is reasonably careful. If a thread is run through before the warps are sent through the machine, it is possible to dye some shades at one end.

Many shades, particularly for cheap goods, are dyed on cotton warps by adding dyestuff solution to the size box. A good red may be obtained by two ends through the sizing machine, whilst creams, lavenders, fawns, pinks, etc., may be finished at one end, though it is not as easy to keep the warps from running off shade as when dyeing in the warp dyeing machine. Direct cotton shades on warps are sometimes matched as nearly as possible in the dye-house, and then topped to shade in the sizing machine. It must be realized that dyeing in the sizing machine is only possible when pure sizing, and cannot be used when the size contains quantities of fillers, such as magnesium sulphate, china clay, etc.

Cotton warps, like cotton hanks, are often dyed in pack machines (see p. 74).

Machine Dyeing.—Machine dyeing for loose cotton, sliver, roving, cops, cheeses, hanks, warps, and beams is being increasingly adopted owing to improvements in the constructions of the various machines designed for this purpose, and to the production of special types of suitable dyestuffs.

Loose cotton, sliver, warps, and hanks may be dyed in the pack type of machine in which the material is packed as uniformly as possible into a detachable perforated cage, and the liquor forced through the pack by means of a centrifugal pump. Cotton hanks may also be dyed in the Hussong machine (see p. 79). Many machines, such as the Longclose, Pornitz, Annicq, Krantz, Franklin, etc., have been designed for the dyeing of cotton in the form of cops, roving bobbins and cheeses, the principle of which is described on p. 77. Beam dyeing, although not widely adopted in this country, is successfully used on the Continent. Special machines for this purpose have been designed by J. Brandwood, Thies, Krantz, Baldwin and Heap, and Obermaier, which are in principle similar to cheese dyeing in that the

yarn is wound on to a perforated beam and the dye-liquor pumped through the package.

When using these machines it should be specially noted that owing to the liquor usually being a short one, less common salt or Glauber's salt is needed in order to exhaust the bath ; moreover, this should be gradually added after the material has been thoroughly saturated with the dyeliquor, so that the dyestuff is not exhausted on to the outside of the material when the assistant is added.

Piece Goods.—From the dyeing point of view cotton piece goods may be divided into those which require to be dyed at full width to avoid creases and cracks on the jigger or padding machine, and those which may be dyed in rope form in the winch machine.

Dyeing in the Jigger.—The jigger is generally used in the dyeing of dark shades on cotton pieces, as the dyebath may be kept more concentrated owing to the small quantity of liquor used in proportion to the weight of the goods to be dyed. When heavy drills and similar materials are to be dyed the use of a jigger with nip rollers attached is strongly recommended, as the dyeliquor is driven into the fibre by the pressure of the squeezing rollers. Only fabrics which do not stretch and which may be wound smoothly selvedge upon selvedge are suitable for dyeing in the jigger as the formation of creases or uneven winding of the selvedges may cause stripy dyeing or dark selvedges. More recently improved designs of tensionless jiggers have minimized these difficulties so that it is now possible to dye more lightly constructed fabrics on them than was formerly possible.

For light shades the bath is prepared with $\frac{1}{4}$–$\frac{1}{2}$ oz. soap per gallon of liquor together with half the necessary quantity of dyestuff. The goods are given one end at a temperature of 60°–70° C., the remainder of the dyestuff then added, and the pieces run from one roller to the other till the desired shade is obtained.

Medium shades are dyed with the addition of : 2–4 oz. Glauber's salt or 1–2 oz. common salt, per gallon of liquor and dark shades with the addition of 4–6 oz. Glauber's salt or 2–3 oz. common salt per gallon of liquor. When dyeing medium and dark shades it is advisable to add the dyestuff first, adding the Glauber's salt gradually towards the end of the dyeing operation : levelling of the shade is thereby much facilitated. Care should

be taken not to add excess of salt when dyeing in the jigger; the bath (cold) should not be more than 6°–8° Tw. when dyeing dark shades.

Dyeing in the Padding Machine.—The padding machine is chiefly employed for dyeing pale and medium shades on light-weight materials. The trough of the machine usually has a capacity of 15–25 gallons, is fitted with 1–3 guide rollers, and should be heated by a steam coil if possible. The temperature of the dyebath should be from 55°–60° C. for light shades, and 70°–100° C. for heavy shades.

The bath is charged with 15–25 gallons water and $\frac{1}{2}$–$1\frac{1}{2}$ lb. common salt or Glauber's salt. About half the necessary amounts of salt, dyestuff, etc., are added and the pieces are given one end. The remaining dye-solution, salt, etc., are added gradually after each end till the desired shade is obtained. When dyeing materials which are difficult to penetrate, it is advantageous to add $\frac{1}{4}$–$\frac{1}{2}$ pint of olein oil or to use one of the new auxiliary products *e.g.* Calsolene Oil, etc., and $\frac{1}{4}$–$\frac{1}{2}$ lb. dextrine to the dyeliquor.

Dyeing in the Winch Machine.—This method of dyeing, which is known as "loose" dyeing to distinguish it from jigger dyeing where the cloth is subject to some tension, is as a rule only adopted for light-weight fabrics, such as voiles, crêpes, knitted goods, etc., although it is sometimes employed for corduroys, velveteens, etc., the pile of which might be injured by dyeing in the jigger. Several pieces are usually dyed together, each piece being sewn at the ends in the form of an endless rope. In this machine the drafts run over a guide roller, through a series of pegs which keeps the several drafts separate and leads them continuously over the winch roller to the dyebath.

The goods are dyed with the addition of 10–20 per cent. Glauber's salt or 20–30 per cent. common salt, calculated on the weight of the pieces. When dyeing in the winch machine there is no danger of the pieces being ended, though they are more likely to be creased and more dyestuff is required, due to increased liquor-material ratio, than when the jigger is used.

Dyeing of Mercerized Cotton.—It may be stated in general that mercerized cotton is dyed with the same dyestuffs and in the same way as ordinary cotton, excepting for the two following reservations :

(*a*) Owing to the increased affinity for direct cotton dyestuffs given to cotton by mercerization, less dyestuff is required to give the same depth of shade than when dyeing ordinary cotton, particularly if the mercerized cotton is not dried before dyeing. Less assistant, which is added more slowly, is also required, *i.e.* the dyeing is carried out more slowly, generally using a higher liquor to yarn ratio than that used for ordinary cotton. Again, light shades are frequently dyed in a soap bath without any other addition, and dried without washing. This entails the use of a little more dyestuff, but this factor is quite negligible compared with the risk of a batch of goods being uneven. It may be said that the affinity of mercerized cotton for direct cotton dyestuffs is between that of viscose rayon and ordinary cotton. The section relating to the dyeing of viscose rayon applies with equal force to the dyeing of mercerized cotton as regards correct choice of dyestuffs, etc., though the mechanical difficulties of dyeing mercerized cotton are much less pronounced than in the case of viscose rayon (see Section XIII.).

(*b*) When mercerized cotton is scrooped after dyeing care must be taken to avoid dyestuffs whose shade would be altered by the acid used in the scrooping.

Scrooping of Mercerized Cotton.—A scroop on mercerized cotton yarn is obtained by working the goods 10–20 minutes in a cold bath containing 10 per cent. soap, wringing out or hydro-extracting without rinsing, and working 10 minutes in a cold bath containing $1-1\frac{1}{2}$ oz. acetic acid per gallon. The scroop so obtained is not as permanent as that which is obtained if tartaric acid is substituted for acetic acid. When using tartaric acid one-third of the above quantity of acetic acid only should be taken. Lactic acid has also been largely adopted as an acid for scrooping purposes with satisfactory results. Sulphuric or other mineral acids should never be used for scrooping purposes, as they are liable to cause tendering, though an examination of some rayon ties has proved that sulphuric acid has been used, with the result that the ties were tender by the time they were exposed for sale

in the retailer's window.   If the mercerized cotton yarn is dyed in a strong soap bath, wrung out without rinsing, and worked in a cold acid bath, the same scrooping effect may be obtained.

The After-treatment of Direct Cotton Dyestuffs.—
Experience has shown that the methods of after-treatment detailed below are of great utility in improving the fastness of some direct cotton dyestuffs to both light and washing.   It cannot, however, be over-emphasized that the methods are not applicable to all members of this class, but only to those which are specifically recommended in the various dyestuff makers' literature   Thus an after-treatment with bichromate is only really effective with those dyestuffs which contain salicylic acid groups, like Chlorazol Green G and Chlorazol Brown M.   The shade of the dyestuffs is usually altered by the after-treatment, for example, the shade of Sky Blue FF when after-treated with copper sulphate is turned much greener.   Reference should also be made to the use of certain auxiliary products which are recommended for increasing the fastness properties of direct cotton dyestuffs (see Section XVII.).

After-Treatment with Copper Sulphate.—This process improves to a remarkable degree the fastness to light of those dyestuffs which are suitable.   A fresh dyebath is charged with $\frac{1}{2}$–2 per cent. copper sulphate, in which the well-washed dyed material is worked 20–30 minutes at 60° C.   In connection with this process it must be remembered that a severe alkaline washing removes the effect of the copper sulphate to a great extent, whereby the shade reverts to the original shade before coppering. Direct cotton blues and browns are largely put through this process, especially the FF Sky Blues and the RW Direct Blues.

A few years ago the Benzo Fast Copper dyestuffs were placed on the market, and have the great advantage over the older dyestuffs which are suitable for after-treatment with copper sulphate in that neither the fastness to light nor shade of the dyeings is impaired, even by repeated washings.   These dyestuffs also give shades which have very good fastness to washing and perspiration.

After-Treatment with Chromium Fluoride or Bichrome.—This process considerably improves the fastness to washing and milling but not to light, of those dyestuffs which are suitable.   A fresh dyebath is charged with 1–4 per cent. chromium fluoride or 1–2

per cent. bichrome, in which the well-washed dyed cotton is worked 20–30 minutes just below the boil. Bichrome has a more marked effect on the shade than chromium fluoride.

After-Treatment with Bichrome plus Copper Sulphate.—In order to improve the fastness of the dyestuffs to light and milling in one operation, it is common practice to work the dyed cotton for 30 minutes at 90° C. in a fresh bath charged with $\frac{1}{2}$–2 per cent. bichrome, $\frac{1}{2}$–2 per cent. copper sulphate and 1–2 per cent. acetic acid. Any cloudiness in the bath must be corrected by addition of more acetic acid before entering the cotton.

After-Treatment with Formaldehyde.—This process increases the fastness to washing and milling, but not to light, of those dyestuffs which are suitable. A fresh bath is charged with 1–3 per cent. formaldehyde (40 per cent.) in which the cotton is worked 20–30 minutes at 60° C. This process is of especial value for most direct cotton blacks, whereby the fastness to washing against white cotton is remarkably increased. The effect of the formaldehyde is most pronounced in the case of those dyestuffs which have an end component with two hydroxyl or two amino groups in the meta position. The formaldehyde combines with the two groups and forms a compound which is less soluble than the original dyestuff, with the natural result that it bleeds less on washing. This type of dyestuff has been largely used in the sewing-cotton trade. It should be noted that most direct cotton dyestuffs are less fast to light when after-treated with formaldehyde than before treatment.

Topping with Basic Dyestuffs.—This is fully dealt with under Basic dyestuffs (see p. 94).

DIRECT COTTON DYESTUFFS WHICH MAY BE DIAZOTIZED AND DEVELOPED

The first member of the direct cotton dyestuffs which could be diazotized and developed was discovered by A. G. Green in 1887, to which he gave the name Primuline. Its shade had no special interest as a direct cotton dyestuff due to its fugitiveness to light. It was, however, discovered that, owing to the presence of a free amino group in the diazotizable position it could be diazotized and developed, and by combining it with various amines and phenols a range of yellow, orange, red, and maroon

shades could be obtained of very good fastness to milling, washing, and boiling acids. This operation can be carried out by first dyeing the cotton with a diazotizable dyestuff, then diazotizing and developing on the fibre. These good properties gradually— because novel methods of application have to gain the confidence of dyers by proving themselves in the manifold uses to which the different classes of goods are subjected—led to the adoption of this process, and Primuline Red (Primuline + B naphthol) became a standard shade. As usual when a new departure in dyestuff chemistry is discovered, it is exhaustively worked by dyestuff chemists, with the result that there is now a large number of diazo dyestuffs available, some of which have outstripped Primuline in importance. The most successful have been the BH type of black, Diaminogene B and Chlorazol Black SD, the consumption of which has been very great for the dyeing of sewing thread and mercerized yarns. The dyeing process is a complicated one, as will be seen below, so that when the sulphur blacks were introduced developed blacks began to lose their importance except for certain lines such as sewing threads, because a much faster black could be obtained with sulphur blacks in a much simpler manner. Owing to the lack of a sulphur red, developed reds were once largely used for reds fast to milling, crabbing, acid cross dyeing, etc., but the intensive development of the azoic reds has materially diminished their importance. One weak point of this class of dyestuff has been the poor fastness to light, but the later additions to this class of dyestuff—Diazo Fast Scarlets—have shown a welcome improvement in this respect. The improved fastness to wet processing of the developed dyestuffs as compared with direct cotton dyestuffs is due to the fact that the dyestuff produced on the fibre after development is insoluble in comparison with the same dyestuff before it is developed. It is only to be expected, therefore, that the shade is faster to wet processing, because the more insoluble a cotton dyestuff is, the faster it is as a general rule.

The main points to remember in connection with this process are :

    1. Stone, wooden, monel or stainless steel vats must be used for diazotizing ; on no account may iron cisterns be used as the diazo compound is thereby destroyed.

2. The diazotized compound is sensitive both to light and heat, either of which decomposes it, so that no delay whatsoever must take place in developing the goods after diazotization has taken place. No sunlight must be allowed to shine on the material, nor must it be put close to a stove or hot steampipe because material so exposed will not subsequently develop. Another point to be watched is to see that there is no leak into the bath from the steam pipe, as this would give local heating of the liquor of the diazo or developing bath which would inevitably cause trouble.

3. Except with naphthylamine ether and amido-di-phenylamine, all developing baths should be on the alkaline side, or the shade will not develop properly.

The material is dyed in the manner already described in the earlier part of this section : it is then well washed and worked 15–30 minutes in a cold bath charged with 1–3 per cent. sodium nitrite and 5–10 per cent. hydrochloric acid, or 3–5 per cent. sulphuric acid. The material is lightly rinsed and passed without delay into the cold developing bath in which the material is worked 15–20 minutes: after which the material is washed, soaped if thought desirable, and dried. Care must be taken to avoid a strong light falling on the material during diazotization or development.

The following developers are the most commonly used : resorcine, meta-phenylene-diamine, meta-toluylene-diamine, B-naphthol and B-oxy-naphthoic acid : naphthylamine ether and amido-diphenylamine are used for blue shades, whilst phenol and α-naphthol are occasionally used. With the exception of naphthylamine ether and amido-di-phenylamine, which require to be dissolved with their own weight of hydrochloric acid, the above developers are dissolved by stirring them into a smooth paste with their own weight of caustic soda, and pouring boiling water over them. With the above two exceptions, all the developers are miscible one with the other in any proportion. This is frequently done, because in the case of blacks, meta-phenylene-diamine gives a black with a brownish cast which may be corrected by the use of some resorcine which gives a green tone black or B-naphthol which gives a blue tone black. It

should be noted that some blacks when developed are less fast to light than when dyed direct.

Shades of good fastness to light and washing are obtained by after-treatment of Primuline with a cold $\frac{1}{4}°$ Tw. sodium hypochlorite solution for $\frac{1}{2}$-hour rinsing, souring, and rinsing again. The after-treatment with sodium hypochlorite never completely oxidizes all the Primuline so that small traces of free Primuline can always be detected by examination of white material which has been treated with soap in presence of Primuline chlorinated. This fact makes it impossible to use Primuline chlorinated for bleaching shades which have to be boiled, although the dyestuff is, naturally, perfectly fast to chlorine. Up to the present time no method has been found whereby Primuline chlorinated can be stripped, so that the correction of faulty shades is impossible.

Wool.—A few direct cotton dyestuffs give shades of excellent fastness to washing and milling on wool, whilst the fastness to light is generally much better than the same dyestuff on cotton. They, therefore, find a limited use in wool-dyeing, e.g. the shawl trade, effect threads in woollen pieces, knitting yarns, etc., whilst a dyestuff like Benzopurpurine 4B is largely used as a scarlet in the low woollen trade. It must, however, be remembered that the majority of direct cotton dyestuffs dyed on wool will stain any cotton or rayon wet processed along with the wool. In dyeing these dyestuffs, a dyebath is prepared with the requisite amount of dyestuff and 10–20 per cent. common or Glauber's salt. The wool is entered lukewarm, raised to boil, and dyed at the boil for $\frac{1}{2}$-hour. To facilitate exhaustion of the dyebath acetic acid may be added, except with Benzopurpurine and dyestuffs similarly sensitive to acid. When after-chroming with chromium fluoride this is added to the dyebath after the bath has been exhausted with acid, and boiling continued another $\frac{1}{2}$-hour. The following dyestuffs are commonly used, Chrysophenine G, Benzopurpurine 4B, Deltapurpurine 5B, Paramine Fast Red F, and Chlorazol Green G.

Silk.—The direct cotton dyestuffs are of great utility in the dyeing of silk when shades fast to milling, washing, or water are required, whilst selected diazo dyestuffs give shades of good fastness to boiling soap, e.g. Primuline developed with B-naphthol is largely used on silk for a red fast to soaping, whilst diazo blacks

are used to dye a fast to milling black on silk noils, which is a form of silk very difficult to dye in fast shades.

Miscellaneous Uses.—The direct cotton dyestuffs are applied to linen and jute in the same way as detailed above for cotton. On the latter fibre they possess good penetrating and fastness to washing properties, although the shades are dull as compared with shades produced with acid and basic dyestuffs.

The direct cotton dyestuffs are not used in dyeing vegetable-tanned leather owing to lack of affinity, but they are gaining increased importance for chrome leather. Dyeing is usually carried out in the drum in which the leather is first drummed with borax in order to remove any acid which may be left in the skin from the chrome tanning process. The leather is then drummed for $\frac{1}{2}$-hour at 40° C. with the requisite dyestuff, with or without the addition of Glauber's salt. Large quantities of direct cotton blacks of the Chlorazol Black E type are used for dyeing chrome leather black.

Wood chip is largely dyed with direct cotton dyestuffs, for which it has a good affinity. Dyeing is carried out at the boil with the addition of Glauber's salt or common salt until the plait is sufficiently penetrated.

Selected direct cotton dyestuffs of good fastness to light are used in the paper trade for shades in which fastness to light is required. Stilbene yellows are largely used on paper, also direct cotton pinks.

Section IX.—THE SULPHUR DYESTUFFS

The sulphur dyestuffs are generally made by fusing together sodium sulphide or polysulphide and organic substances, usually organic nitrogen compounds. As their colloidal nature has prevented their isolation in a pure state little is known of the reactions involved in their preparation or of their constitution.

The earliest known type of this class of dyestuff was Cachou de Laval (C.I. 933) discovered by Croissant and Bretonnière in 1873. Although it possessed properties of great value to the cotton dyer, it remained the sole representative of the sulphur dyestuffs until Raymond Vidal—a French chemist—discovered Vidal Black in 1893. This dyestuff was at that time novel in its application and outstanding in its fastness to light, milling, washing, and boiling acids—far surpassing any cotton black known to cotton dyers with the exception of Aniline Black produced on the fibre by the oxidation of aniline oil or salts. Vidal's discovery aroused the greatest interest, both in dyestuff making and dyeing circles, with the result that the fusion of organic bases with caustic soda and sulphur, etc., was so intensively and successfully worked that the range of sulphur dyestuffs is now extremely large and includes blacks, blues, greens, browns, maroons, oranges, and yellows. There are, however, some notable gaps in the series before the range may be considered complete : at the time of writing no bright scarlet or crimson has been commercially produced.

It is a curious fact that if the first representative of a new class of dyestuff is of exceptional fastness it is concluded that all members of this class possess the same exceptional fastness, and it is only by bitter experience that individual dyestuffs are estimated at their true value. This mistake was made in the case of the sulphur dyestuffs, and has been repeated in recent years in the case of vat dyestuffs. With few exceptions no sulphur dyestuff is as fast to light as the sulphur blacks ; some sulphur

blues and greens, such as Thionol Green B—possess similar fastness, but sulphur browns, olives, and oranges cannot be compared with the sulphur blacks for fastness to light, whilst the sulphur yellows are notably deficient in fastness to light. Some of the more recent dyestuffs show improved light fastness, *e.g.* Immedial Dark Brown B. To overcome the deficiency of the yellows it is a very common practice of dyers to use a direct cotton yellow of the Chlorazol Fast Yellow B type. Such yellows possess excellent fastness to light—much superior to sulphur yellows—together with very good fastness to milling and washing, except against white cotton, so that their use is permissible and advisable except when the dyed shade has to withstand a subsequent boiling with acid, *e.g.* cotton warps which are cross dyed. Although the type of direct cotton yellow mentioned will withstand the reducing action of sodium sulphide, it must be remembered that the majority of direct cotton dyestuffs are destroyed by this treatment. It must also be remembered that the sulphur dyestuffs are peculiarly sensitive to the action of chlorine and hypochlorites. In this respect, however, Indo Carbon CL is exceptional in being sufficiently fast to be recommended for shirting stripes.

The virtues of the sulphur dyestuffs immediately forced themselves on the notice of the dyers, but their method of application was so novel that they were looked upon with diffidence. Some of the earliest dyeings on the large scale were very discouraging, but these early difficulties were gradually overcome by the co-operation of the dyestuff makers and the master dyers. Nowadays the dyeing of sulphur dyestuffs is thoroughly understood, and few difficulties are encountered.

Side by side with the improvement of the methods of application must be recorded improvements in the methods of manufacture, notably in the case of the blacks. The earliest types of sulphur blacks, such as Vidal Black, possess inferior colouring power and affinity for cotton as compared with modern types, and in order fully to develop the shade it was necessary to chrome them. Modern sulphur blacks do not, however, require chroming, and indeed are practically never chromed except in the case of warps, and for material in which extreme fastness is required, such as guaranteed washing fabrics. In the early days of sulphur dyestuffs their use was confined to raw cotton, hanks, and warps

owing to the rapidity with which the earlier types oxidized, making the level dyeing of pieces impossible due to the rapid bronzing of the selvedges. Nowadays, however, an enormous number of cotton pieces are dyed without any trouble in the ordinary routine of the cotton piece dyehouse.

Several processes have been patented for the dyeing of silk, wool, and mixed goods. On silk they may prove useful for shades fast to boiling, but their general lack of brightness limits their use for this class of work. The authors are of the opinion that there is practically no scope for their application on all-wool goods because of the large number of satisfactory fast wool dyestuffs, which are not only faster than the average sulphur dyestuff, but whose application is easier and which leave the wool in better condition. For instance, there is no comparison in the ease of dyeing a worsted piece with Diamond black compared with dyeing a similar piece with sulphur black.

With the exception of the black it is advisable to avoid the use of sulphur dyestuffs on continuous filament viscose rayon excepting when the fastness compels their use on price grounds. They are the most uneven-dyeing class of dyestuffs on rayon of varying dyeing affinity as there are practically none which may be classified as even-dyeing, whereas every other group of dyestuffs has, at least, some members which are even-dyeing. It must also be remembered that after-treatment of rayon with metallic salts is not advisable because this renders the fibre sticky and resistant to sizing. This inability to use metallic salts for after-treatment makes matching to shade more than usually difficult owing to the gradual change of shade as oxidation becomes complete, whilst it is impossible to give the same degree of fastness as on cotton which can be after-treated with metallic salts. Again, rayon yarn dyed with sulphur dyestuffs frequently has a harsh handle so that it must be softened or the winding properties of the yarn will be depreciated. Unfortunately, rayon dyed with these dyestuffs is frequently required for fast to cross-dyeing warps which have to be sized, and the soap or soluble oil used to soften the yarn makes it resist the absorption of the amount of size necessary to make a good weaving yarn. Experience has also shown that effect threads of rayon dyed with sulphur dyestuffs are apt to act as a mordant for many of the acid dyestuffs, with the result that the

desired shade of the effect threads as dyed is frequently altered during the cross-dyeing of the wool.

No theory has been advanced as to the mechanism of the dyeing of sulphur dyestuffs on cellulose. It has been shown, however, that the leuco compounds of the vat dyestuffs behave like direct cotton dyestuffs and dye cellulose by a process of absorption followed by diffusion (see p. 188), so that it is a problem worthy of investigation to see if the same mechanism applies to the dyeing of sulphur dyestuffs. These dyestuffs may be brought into perfect solution by means of sodium sulphite, but in this form have no affinity for cotton, and must be reduced to the alkali-soluble leuco form before they possess any affinity. This may be accomplished by alkaline reducing agents, but the one universally used is sodium sulphide, owing to its extreme suitability and cheapness. Two qualities of sodium sulphide are used in practice : sodium sulphide, crystals and the quality known as concentrated or " rock " sulphide which is double the strength of the crystals. For use in pack dyeing rock sulphide should be examined for insoluble matter since some brands contain much more than others.

Sulphur Black Tendering.—One of the greatest objections to sulphur dyestuffs, more especially blacks, is that the dyed cotton is liable to tender on prolonged storage, particularly after acid cross-dyeing. In every case the tendered fibre is found to contain free sulphuric acid apparently derived from the oxidation of decomposition products of the dyestuff. A considerable amount of work has been done on this subject, mainly during the years 1900–1914, with a view to determining the conditions which favour tendering and methods for preventing its occurrence (*e.g.* Pilling, *J.S.D.C.*, 1906, p. 54) but a perfectly satisfactory explanation of this defect has not yet been given.

Investigations have shown that an after-treatment with bichrome followed by rinsing reduces the danger of tendering by forming and removing the oxidation products before the material is stored. After dyeing and rinsing, the material should be given an alkaline finish in a liquor containing 5 gms. per litre sodium carbonate or other mild alkali and dried without rinsing in order to neutralize any mineral acid as it is formed. The protective action of such soluble alkalies does not, of course, persist after the material has been washed. Experience has also shown that sul-

phur blacks after-treated with copper sulphate are more rapidly
tendered than those which have not received this treatment, so
that it should never be used. This is to be regretted since such
an after-treatment vivifies the shade of many sulphur black
dyeings. Again, goods which have subsequently to be stoved,
i.e. bleached by means of sulphur dioxide, must not contain any
material dyed with sulphur black, as this process accelerates
tendering to a surprising degree. Dyers are, therefore, accus-
tomed to use for this purpose direct cotton dyestuffs developed.
In recent years sulphur blacks have been introduced, such as the
Indo carbons, which are stated to be practically free from the
risk of tendering on storage.

The following notes abstracted from the published work of
Dr. Zanker and his collaborators deal with a long series of experi-
ments on the causes of the tendering of sulphur black dyed cotton.
The first experiments were carried out in 1913 (Zanker and Wey-
rich, Lehne's " Farber Zeitung," 1913, p. 479) and further results
have been published at intervals since then. The authors con-
sider this work to be a valuable contribution to the researches
already carried out by other investigators.

The method recommended for determining whether a sulphur
black will tender or not is as follows. Dyed samples of equal
depth are heated for 1 hour in an oven at 140° C. The hanks
are then taken out and allowed to lie in the atmosphere till
they have taken up the normal amount of moisture. They are
then re-heated for a further hour to 140° C., taken out and tested.
It is essential to carry out the work in the manner described
because the moisture plays a definite part in the tendering. In
every heat test a blank experiment should also be made with
undyed cotton yarn in order to make certain that no tendering
of the cotton is caused by the high temperature alone. The rate
of tendering is indicated in the following table, which shows the
action of temperature in promoting tendering. Samples from the
same dyeing exposed to the following temperatures took the stated
lengths of time to reach the same state of tendering.

Ordinary room temperature	$1\frac{1}{2}$ years
40°–50° C.	.. 10 months
60° C.	.. 4 ,,
80° C.	.. 1 ..

100° C. ..	..	..	..	..	.. 72	hours
120° C. ..	..	..	..	..	.. 31	,,
140° C. ..	..	..	..	..	.. 2	,,
160° C. ..	..	..	..	..	.. $1\frac{1}{2}$	,,

In every case free sulphuric acid was found in the cotton, and since all yarns before testing were extracted with carbon bisulphide, the acid was not produced from free sulphur attached to the fibre.

The above method of testing has been in use for many years and has been found to give reliable tests as to the liability of any special sulphur black to cause tendering.

The following method is used to determine the amount of total sulphur present in any sulphur black : $2\frac{1}{2}$ gms. of the dyed material to be tested are put in a beaker with 75 c.c. of bleaching liquor at 3° Tw., completely free from sulphate. The cotton is left in this liquor until it is bleached completely white, then squeezed out and immersed in a further 50 c.c. of bleaching liquor for 1 hour at 30°–40° C. By this means the last trace of sulphur is quantitatively converted into sulphuric acid. The cotton is then washed 5 times with boiling distilled water, and the washing added to the bleaching liquor. The total liquor is then evaporated down, acidified with pure hydrochloric acid, and the solution boiled in order to remove all the chlorine. The sulphuric acid is then precipitated by the addition of barium chloride, and estimated as barium sulphate.

Four different estimations on one and the same dyed material gave the following results :—

Determination	S calculated as SO_3	S calculated as sulphuric acid
1	2·56	1·023
2	2·67	1·070
3	2·65	1·068
4	2·59	1·031

The quantitative estimation of sulphuric acid in a sulphur black dyeing was carried out as follows : The material was heated for 2 hours at 140° C. according to the method already described, when it was found that the formation of sulphuric acid, even after heating 1 hour, was so considerable as to cause the yarn to depreciate 65 per cent. in its breaking strength. After the cotton had been heated as above, it was put into an

excess of caustic soda 1/100 normal solution. The caustic soda solution was then back titrated and the amount of sulphuric acid thus determined. As a control experiment the sulphuric acid formed was also determined by precipitation with barium chloride : the figures were found to agree with the caustic soda method.

By this method the following results were obtained :

Determination	S calculated as sulphur
1	0·223
2	0·227
3	0·220
4	0·227

The amount of unchanged sulphur still left on the fibre was then determined by the bleaching liquor method already detailed :

Determination	S calculated as sulphur
1	0·742
2	0·700
3	0·731
4	0·743

To show how close the total of changed-by-heat test and unchanged sulphur corresponds with the total weight of sulphur found on the dyeing, the following table is given :

Determination	Total of changed and unchanged sulphur	Total sulphur
1	0·965	1·047
2	0·927	1·027
3	0·960	1·045
4	0·970	1·020

The next experiments were carried out to determine whether a longer heating than 2 hours as already described would convert more of the sulphur shown to be unchanged by this heating into sulphuric acid, because the above tables show that the proportion of sulphur which can be converted into sulphuric acid by heating at 140° C. has a definite relation to the total amount of sulphur present. This relation is 1 of convertible sulphur to 4·5 of total sulphur present. Dyeings were heated for 14 days at 60°–70° C., allowing every now and again the yarn to take up its natural moisture. Although the yarn by this treatment was

completely destroyed, the total amount of sulphur converted into free sulphuric acid was not increased by this prolonged heating. These experiments, therefore, give the definite result that heating at 140° C. for 2 hours is sufficient completely to convert all sulphur in the sulphur black which is convertible by this method into sulphuric acid. In other words, the sulphur that is converted into sulphuric acid and causes tendering is only a definite proportion of the total sulphur contents of the sulphur black. Repeated experiments made with many sulphur black dyeings have confirmed the above results.

In carrying out experiments with the actual dyestuff, as distinct from the dyeings, great difficulty was found in purifying the dyestuff. The following method was carried out : 50 gms. of commercial sulphur black were boiled in 2 litres of distilled water, and dilute acetic acid was then added to the solution until complete precipitation of the dyestuff showed itself by spotting on filter paper. The precipitates so obtained could not be filtered, but by boiling for a quarter of an hour gradually coagulated until washing and filtering was quite possible. The precipitate was then washed until free from sulphate and chloride. By this method 40 per cent. of so-called pure dyestuff was obtained from the commercial dyestuff, having an ash content of 1·4 per cent., which consisted of alkali. The total amount of sulphur determined in this pure dyestuff amounted to 33 per cent.

For a complete conversion of convertible sulphur into sulphuric acid, the purified dyestuff was heated at 140° C. till no increase in the acid contents took place. In a series of experiments the quantity of acid formed amounted to 8·1 per cent. Calculated as sulphur this gave a proportion of 1 part of convertible sulphur to 4·1 per cent. total sulphur content, agreeing very well with the results obtained by similar treatment of the dyeings, the result in that case being 1 to 4·5.

In the experiments for the conversion of the convertible sulphur in the dyestuff into sulphuric acid it was noticed that the least traces of heavy metals played a very distinct part in the ease with which the sulphur was converted into sulphuric acid. If the dyestuff was purified so that there only remained in the ash small quantities of alkali, the sulphur dyestuff had to be heated 6 times to 140° C. in order to convert the convertible sulphur completely

into sulphuric acid. On the other hand, if the least trace of heavy metals, such as iron, was present, the convertible sulphur was converted into sulphuric acid by only once heating to 140° C., the total amount of sulphur converted being the same in each case. In order to determine the influence of salts on the formation of sulphuric acid in sulphur dyestuffs, several samples of purified dyestuff were mixed with sodium bicarbonate, sodium acetate and cream of tartar, in addition to traces of iron salts. They were heated 4 times for $1\frac{1}{2}$ hours in damp air to 140° C. All additions accelerated the formation of acid. As is already known, acid reacting salts and traces of acid were also found to accelerate the production of sulphuric acid. These results show that the action of an after-treatment with sodium acetate is solely effective in so far as it neutralizes any acid that is formed, as the after-treatment does not prevent the formation of sulphuric acid. Indeed the above experiments definitely show that it accelerates the formation of sulphuric acid.

In order to prevent a subsequent conversion of the convertible sulphur on the fibre into sulphuric acid, experiments were carried out to oxidize this sulphur before dyeing. All experiments, however, showed that dyestuffs treated in this way lost the greater part of their valuable dyeing properties, and that the more sulphur that was oxidized, the less soluble did the dyestuff become. The convertible sulphur in sulphur black dyestuffs is, therefore, absolutely necessary for the formation of a good black.

The chief results of Zanker's work may be summarized as follows : After removal of free sulphur by extraction with carbon bisulphide, 20–25 per cent. of the sulphur in a sulphur dyestuff exists in a special chemically active and easily oxidized form, and is present on the fibre in the same form. Owing to its very fine state of division in the cellulose fibre it is easily oxidized and causes tendering. The remaining 80 per cent. of the sulphur can only be oxidized to sulphuric acid by such a strong treatment that the dyestuff is completely destroyed. Sulphur, therefore, in sulphur blacks is present in three forms :

1. Mechanically free sulphur, extractable with carbon bi-sulphide.

2. Easily oxidizable, chemically active sulphur, which by heating the dry dyestuff or the actual dyeing in the

presence of air, is easily converted into sulphuric acid. This quantity amounts to 20–25 per cent of the total combined sulphur contents.

3. Firmly combined or stable sulphur, only oxidizable by strong oxidizing agents, entailing complete destruction of the dyestuff. This quantity amounts to 75–80 per cent. of the total sulphur contents, and plays no part in the tendering.

APPLICATION

Sulphur dyestuffs should be stored in a cool dry place and the cover of the container replaced immediately after any dyestuff has been withdrawn, as they deteriorate rapidly by oxidation if exposed to the atmosphere. Again, all brass and copper fittings should be substituted by Monel metal, stainless steel, iron, or lead fittings owing to the action of sodium sulphide on the copper.

Dissolving.—The best way to dissolve sulphur dyestuffs is to mix the dyestuff and soda ash into a smooth paste with cold water, add the sodium sulphide, pour boiling water over the paste, and boil with a loose steam-pipe for 5–10 minutes. The object of stirring the dyestuff into a paste with soda ash before adding the sulphide is to neutralize any slight acidity of the dyestuff, so preventing the acid from acting on the sodium sulphide. If the sulphide and soda ash are added together, the acid attacks the sulphide in preference to the soda ash, and tends to give a less satisfactory solution of the dyestuff. The above method of dissolving is undoubtedly the best, but it must be admitted that in many dyehouses the dry dyestuff, sulphide and soda ash are thrown into the dyebath and dissolved by boiling the bath up for 10 minutes. The solubility of the sulphur dyestuffs varies considerably according to their method of manufacture, because the finished product in some cases contains a little sodium sulphide, whilst others contain none. The amount of sodium sulphide required for each individual dyestuff may be determined by experiment, but the dyestuff manufacturers usually save the dyer this trouble. It is preferable to dissolve sulphur dyestuffs in wooden or enamelled iron vessels and not iron vessels, as it is the authors'

experience that improved results are obtained by avoiding the use of iron vessels for sulphur dyestuffs.

As the sulphur yellows are the most insoluble of the sulphur dyestuffs, special care should be taken in dissolving them or the maximum colour value of the dyestuff is never obtained. It is of the highest importance to dissolve sulphur yellows in a very concentrated solution of sodium sulphide, therefore the method recommended above should be used, because proper value will not be obtained by throwing the dry dyestuff in the dyebath. The most certain way is to stir them into a paste with their own weight of caustic soda, then to add the sodium sulphide and a little water, and boil till complete solution is obtained.

DYEING

In general the sulphur dyestuffs are dyed at or near the boil, but with a few dyestuffs lower dyeing temperatures are recommended, e.g. Thionol Sky Blue 6BS and Sulphol Red Brown are best dyed at 50° C. The affinity of the leuco compound of the sulphur dyestuffs for cotton is not very great, but it is increased by the addition of common salt or Glauber's salt, which helps to exhaust the dyebath. Common salt is most frequently used, but Glauber's salt is preferred by some dyers, particularly when dyeing fine yarns. The dyebaths are not exhausted, even when salt is added, so that when possible dyebaths are worked continuously in order to avoid running dyestuff down the drain, i.e. the dyebaths are kept what is termed " standing." Such dyeliquors require less dyestuff additions than a new bath, so effecting economy of dyestuff. There is a limit to the length of time a sulphur dyebath should be kept standing, which naturally depends on the number of dyeings put through, but such a dyebath should not be kept longer than 3 months without letting off and cleaning out. The authors have met with sulphur black dyebaths which had been kept for 2 years without letting off, with the result that the dyeings were very dirty, due to the accumulation of dirt in the dyebath ; each dyeing of cotton leaving a certain amount of dirt in the bath. In order to avoid using an excess of salt in a standing bath the liquor should be tested cold by means of a hydrometer, the bath should not register more than 8°–12° Tw.

Should a bath register more than this, salt should be omitted till the density of the bath has been reduced to 8 Tw. Since, however, the average dyehouse has not sufficient cisterns to reserve one for each dyestuff, the usual result is—except in the largest dye-houses—that sulphur black dyebaths only are kept standing.

The method published by Whittaker ("Dyer and Calico Printer," 1916, p. 50) for exhausting baths of sulphur dyestuffs should be borne in mind. Dyeing experiments showed that the addition of ammonium sulphate, chloride, formate, acetate, or the corresponding amount of free acid to a sulphur dyestuff dye-bath exhausted the dyebath. The following tests illustrate the method. Two dyebaths were prepared as follows :

Bath 1	*Bath 2*
18 per cent Thionol Black BX	12 per cent Thionol Black BX
18 per cent sulphide conc.	12 per cent sulphide conc.
5 per cent soda ash	5 per cent soda ash
60 per cent salt	60 per cent salt

The yarn was entered in the boiling dyebath, worked $\frac{1}{2}$ hour, 5 per cent ammonium sulphate added to Bath 2, and dyeing continued for a further 15 minutes. Equal depth of shade was obtained from the two dyebaths, Bath 2 being completely exhausted. The amount of ammonium salt or free acid added must be so regulated that the bath remains alkaline throughout.

In dyeing with sulphur blacks a white scum often collects on the top of the liquor, and causes trouble by attaching itself to the cotton, causing white marks. This white scum is due to finely divided sulphur, and may be prevented by adding sodium sulphite, which dissolves the free sulphur, to the dyebath. Any goods which show these white marks can also be immediately put right by a treatment with hot sodium sulphite solution. Many people have expressed the fear that these marks would cause tendering, but this fear is groundless, since free sulphur has no influence at all on the liability to tender on storage (see p. 153).

One of the commonest occurring faults, particularly with sulphur blacks and blues, is bronzing of shade, which may be caused by :

    1. Faulty manipulation or excessive delay between lifting the material out of the dyebath and washing off, *e.g.* letting unwashed material lie during a dinner hour.

2. Excess of dyestuff on the material through having too
   strong a dyebath, or too much salt, so overloading the
   fibre with dyestuff.

3. Shortage of sodium sulphide so that the dyestuff is not
   in good solution, and only dyes on the surface of the
   material, where it is quickly oxidized by contact with
   the atmosphere.

Bronziness is most easily removed by treating the cotton
with oil emulsion as detailed under " Softening." If the use of
oil is objectionable for any particular goods, treatment with a
boiling soap solution, or a strong sodium sulphide solution is the
next best remedy.

Uneven shades, unless very pronounced, may be corrected by
treatment with a warm sodium sulphide solution : if this is not
sufficiently effective, the shade should be bleached with hypo-
chlorite, or, alternatively, stripped with alkaline sodium hydro-
sulphite. With some sulphur dyestuffs permanganate bleaching
is very effective.

LOOSE COTTON.—The dyeing of loose cotton with sulphur
dyestuffs is carried out on an extensive scale owing to the ease
with which shades fast to light and milling, suitable for mixture
with wool and shoddy for cheap suitings, etc., can be obtained.
For this class of work the redder shade sulphur blacks are used,
not the brighter and greener shades, which are mainly used for
fine yarns and pieces. The paste or liquid forms of sulphur black
are most largely used for loose cotton; these possess ready solu-
bility, but are less concentrated than the powder forms. The
application is extremely simple. A boiling dyeliquor is prepared
with the requisite dyestuff, sodium sulphide and soda ash, and
the unboiled cotton thrown in and boiled under. Common salt
is then added, poleing continued for $\frac{1}{2}$ hour ; the cotton is allowed
to feed in the simmering bath for at least $\frac{1}{2}$ hour, when, unless
the cistern is required, the steam is shut off and the cotton allowed
to feed in the cooling bath. In the case of blacks, the work is
usually so arranged that two lots are dyed in 24 hours—one lot
being put in at the end of the day, and taken out first thing in
the morning, another lot put in straight away and taken out in
time to get the lot in for the night. Seeing that the one done in
the daytime is not as long in the dyebath as the one left over-

night, some dyers, if working on a 10 per cent. standing bath, charge the bath with 11 per cent. in the morning and 9 per cent. in the evening, so as to counter-balance the longer time in the bath of the one left overnight. A considerable economy in dyestuff and labour will be effected if a tank fitted with an ejector is placed under the dyebath into which the dyeliquor may be run after dyeing. The first rinsing may also be run into the supply tank. If the dyebath is also provided with a valve leading into the drain, the cotton may be washed and after-treated without removing it from the cistern in which it has been dyed, thereby saving time and labour.

The following quantities are typical of a dyebath for loose cotton :

1st Bath	*2nd Bath*
15 per cent sulphur black powder	14 per cent dyestuff
15–30 per cent sodium sulphide conc.	14 per cent sodium sulphide conc.
5 per cent soda ash	2 per cent soda ash
60 per cent common salt	40 per cent common salt

3rd Bath	*Standing Bath*
13 per cent dyestuff	12 per cent dyestuff
13 per cent sodium sulphide conc.	12 per cent sodium sulphide conc.
2 per cent soda ash	2 per cent soda ash
20 per cent common salt	10 per cent common salt.

It is a good practice to use an excess of sulphide in the first bath to ensure that the dyestuff will be in perfect solution, which is why 15–30 per cent. is used above.

Cotton Hanks.—The hanks are first boiled out with alkali, in an ordinary low-pressure kier, but if a kier is not available the bundles of yarn may be placed in canvas bags and boiled 8–10 hours in an open cistern. This long boiling is specially necessary when dyeing fine two-fold weft yarn. When dealing with yarns containing cotton seeds it is essential to kier boil with caustic soda under pressure in order to ensure their removal as they are not removed by boiling in a cistern without pressure. For yarns the greener and brighter sulphur blacks are used, except in cases of backing yarns for which depth rather than beauty of of shade is required. Yarn does not require so much dyestuff as loose cotton, so that the dyebaths are charged as follows :

1st Bath	*2nd Bath*
10 per cent sulphur black	9 per cent dyestuff
10 per cent sodium sulphide conc.	9 per cent sulphide conc.
5 per cent soda ash	2 per cent soda ash
40 per cent salt	30 per cent salt

3rd Bath	*Standing bath*
8 per cent dyestuff	7 per cent dyestuff
8 per cent sulphide conc.	7 per cent sulphide conc.
2 per cent soda ash	2 per cent soda ash
20 per cent salt	10 per cent salt

In the early days of sulphur dyeing on yarn, bent sticks were used in order to prevent oxidation of the dyestuff on the yarn during dyeing ; nowadays, straight sticks are practically always used. The yarn is entered into the hot bath, given two turns, steam is turned on, and the yarn worked for $\frac{3}{4}$–1 hour at the gentle boil. As previously stated, Glauber's salt is preferred to common salt by many dyers, especially for fine yarns ; which assistant to use must be decided by the individual dyer according to the class and quality of work required. For fine yarns and hosiery, the best results are obtained by using no assistant, but a larger percentage of dyestuff is required.

Cotton Warps.—Owing to the fact that sulphur dyestuffs will withstand the crabbing, steaming, and boiling with acids to which may warps are subsequently subjected, they are largely adopted for this class of work.

Before dyeing it is advisable to boil out the warps as follows :

1st Box—Cold caustic soda liquor 10°–15° Tw.
2nd and 3rd Boxes—Boiling water
4th Box—Cold running water

In the dyeing machine the dyestuff boxes are charged with :

2 lb. sulphur black
2 lb. sodium sulphide conc. } per 10 gallons
$\frac{1}{2}$ lb. soda ash   liquor
1$\frac{1}{2}$ lb. common salt }

Subsequent dyeing requires the addition of :

6 per cent sulphur black
6 per cent sulphide conc. } Calculated on the weight
$\frac{1}{2}$ per cent soda ash   of warp
2 per cent common salt }

In accord with the tendency in all dyeing operations to increase production and save time and labour, large warp machines containing 12 boxes are used, in which it is possible to dye warps a full black at one run.

The boxes are arranged as follows :

Boxes 1–4 contain boiling dyestuff
Boxes 5–6 contain running water
Boxes 7–8 contain chrome (if necessary)
Boxes 9–11 contain running water
Box 12 contains dilute soda, soap or ammonia

When dyeing in the long machine the dyestuff is not all added to the dyebath at the beginning, but in the following manner : the first boxes are filled with dyestuff solution mixed in the proportions previously given.   The chrome boxes are filled with the necessary liquor, and a thread or hank is tied on to the string, which is then run through the machine.   If the hank or thread is full enough the warps are tied on, and the machine is started. Running off shade is prevented by feeding in stock solution from an overhead tank.   The stock liquor is made up as follows :

> 10 lb. black
> 100 lb. sulphide conc.
> 60 lb. common salt
> 25 lb. soda ash
> 100 gallons of water

If the stock solution is made up in this way each gallon of liquor will represent about 1 lb. of dyestuff, and thus the amount of dyestuff added may be easily regulated.   The speed of the long machine should be so arranged that any given point on the warps is in contact with the dyeliquor for 3–3½ minutes.   When dyeing sulphur dyestuffs in a warp machine it is advisable to have the top rollers fixed below the level of the liquor—all fear of bronziness and unevenness is then avoided.   The fittings, bearings, steam coils, etc., must all be made of iron, as copper is attacked by sodium sulphide.

Piece Goods.—Sulphur dyestuffs are successfully dyed on piece goods on an ordinary jigger, a jigger fitted with nip rollers, or on the continuous dyeing machine, though the latter is only suitable for big runs of one shade, usually black.

When dyeing on the jigger it is advisable to dye pieces of the same width together and to see that the cloth is rolled on to the beam of the jigger with the selvedges straight and smooth.   If this is not done the selvedges are liable to be dyed darker than the body of the cloth, so giving an unsatisfactory result.   It is sometimes possible to clean up the selvedges by treatment in a fresh bath with sodium sulphide, whilst if one-third of the sodium

sulphide of a mixture of caustic soda and glucose is used in dyeing, the tendency for dark selvedges is reduced.

For piece goods the greenest and brightest sulphur blacks are used, because all sulphur blacks redden in the finishing processes. The pieces are first boiled out with alkali to remove size, etc., and are then batched on to the roller.

The dyebath is charged with :

2 lb. sulphur black	
2 lb. sodium sulphide conc.	per 10 gallons liquor
½ lb. soda ash	

Then :

6-8 per cent. dyestuff	
6-8 per cent. sodium sulphide conc.	calculated on the weight of the pieces
2 per cent. soda ash	

It is advisable to run the piece through the boiling dyebath before the dyestuff is added ; this ensures that the cloth is hot as it enters the dyebath instead of being cold and so lowering the temperature of the dyeliquor. It is also advisable to pour some of the dyeliquor over the guiding rollers before setting the jigger in motion : the pieces are given 6-8 ends in the simmering liquor. The dyestuff is not added all at once, but half is given at one end, then the remaining half at the second end. When dyeing sulphur blacks on pieces the addition of salt is not recommended as it reddens the shades considerably, and there is a greater tendency for the selvedge to bronze when salt is present. Cotton pieces with worsted border in which the cotton is usually mercerized must be dyed cold to leave the wool white, and glue added to the dyebath to preserve the wool from injury as per the following recipe :

1st Bath	Standing bath
12 per cent. sulphur black	8 per cent. sulphur black
8 per cent. sodium sulphide conc.	5 per cent. sodium sulphide conc.
12 per cent. soda ash	¾ per cent. soda ash
¾ per cent. brown gum	½ per cent. glue
20 per cent. Glauber's salt	8 per cent. Glauber's salt

Protectol Dekol and other sulphite cellulose waste liquors have been put upon the market as chemicals which will preserve wool from injury in the presence of alkalies and alkaline sulphides.

The recipes given above have all related to sulphur blacks, but the sulphur blues, green, etc., are all dyed on similar lines, though the dyestuffs, apart from the blacks, are used in varying percentages according to the shade being dyed.

Machine Dyeing.—The principle of dyeing sulphur dyestuffs in pack machines is the same as described above, though great care must be taken to see that the dyestuff is in perfect solution, so that it is usual to increase the amount of sodium sulphide when dyeing in machines. Moreover, since less liquor is usually employed in machine dyeing the quantity of salt added is considerably reduced or completely omitted.

In dyeing, the liquor is circulated through the material for 15 minutes without steam, and the temperature of the liquor raised to the boil for 1 hour. The material is then given three washes, a little Turkey Red Oil being added to the final wash liquor.

The After-treatment of Sulphur Dyestuffs.—The following methods of after-treatment are frequently used in conjunction with the sulphur dyestuffs.

Topping with Aniline Oil.—This method is confined to sulphur blacks, and is used to obtain a shade of black which is denser than the shade obtainable with sulphur blacks alone. Moreover, the blacks so obtained are faster to milling, whilst the cotton is also weighted by the process.

The following recipe will be found to give good results, though it may be varied within wide limits, *e.g.* the quantity of aniline, etc., may be increased so as to yield a darker shade. The bath is made up as follows : 8 per cent. bichromate is dissolved in boiling water and added to the cold dyebath, next 4 per cent. iron liquor, then 4 per cent. D.O.V., finally 4 per cent. aniline oil, and 4 per cent. spirit of salts, previously mixed together in a bucket, along with a little water to keep down the fumes. The bath is stirred up, and the sulphur black dyed cotton is entered, worked $\frac{1}{2}$ hour cold, raised up to 90° C. in $\frac{1}{2}$ hour, lifted out, and well washed off.

After-Treatment with Metallic Salts.—The two salts used are bichromate and copper sulphate alone and together, the former improving the fastness to milling, the latter the fastness to light, but must not be used with sulphur black for reasons already stated (see p. 154). The method of treatment is as follows—a fresh bath is charged with :

1–3 per cent. bichrome, 1–3 per cent. D.O.V. ; or
1–3 per cent. bichrome, 1–3 per cent. acetic acid ; or
1–3 per cent. bichrome, 1 per cent. copper sulphate, 2 per cent. acetic acid

and the cotton worked in the above for half an hour at 60° C.

To prevent the formation of dark stains due to precipitation of copper sulphide from any residual sulphide in the washed material, it is important to add the copper sulphate after adding the acetic acid and bichrome.

Cotton after-treated by any of the above methods must be thoroughly washed to remove every trace of acid. To make certain of this, 1 lb. soda ash may be added to the last wash water.

After-Treatment with Sodium Perborate.—This method of after-treatment is useful for the sulphur blues, and has the effect of considerably brightening the shades. An after-treatment with perborate will be found very useful for oxidizing all sulphur dyestuffs and so approximating to the final shade when oxidation is complete. Unfortunately, shades so oxidized are never as fast as shades which have not been after-treated. This is particularly noticeable when testing the fastness to perspiration.

Softening or Oiling.—After dyeing, the dyed cotton is some-times softened with one of the new auxiliary products or with an oil emulsion made as follows : 100 lb. palm oil are melted in an iron pan, 12 lb. caustic soda, 90° Tw. are added, and the mixture is well stirred, covered up and left overnight, the heat being usually sufficient for saponification of the oil. When saponification is complete a sample should emulsify completely in water, without any oil separating on the surface. Ten per cent. of the above is applied to the cotton in a bath at 60° C., when the cotton will practically absorb all the oil, giving it a soft handle ; the shade of the black is also improved due to the removal of any bronziness of the shade.

Topping with Basic Dyestuffs.—Sulphur dyestuffs possess a great affinity for basic dyestuffs ; in fact they act as a mordant for them, the resulting shades possessing quite a good fastness to washing. This process is, therefore, frequently used for vivify-ing shades dyed with sulphur dyestuffs, but the operation must be carried out carefully, as the basic dyestuffs have a tendency to rush on unevenly. The dyed cotton must first be washed thoroughly in order to remove any alkali and sulphide as com-pletely as possible. The cold topping bath is then charged with 5 per cent acetic acid or alum, the cotton worked in this, the requisite dyestuff added and the temperature of the bath gradually raised until the dyestuff is exhausted.

The Immedial Leuco Dyestuffs.—These dyestuffs consist of a group of sulphur dyestuffs marketed as their leuco compounds which can be dissolved and dyed without the addition of sodium sulphide. They have a good affinity, using salt as the assistant, when dyed from a cold dyebath, and are stated to be very suitable for yarn, package, and piece dyeing of all vegetable fibres, including rayon ; the purity of these dyestuffs as compared with the ordinary sulphur dyestuffs makes them particularly suitable for package dyeing. Solutions of these dyestuffs are prepared by pasting the dyestuffs with a little water at about 30° C. diluting with 10–20 times the quantity of water, and allowing to stand for 10 minutes. The dyestuff is then added to the dyebath containing soda ash and common salt. When dyeing light or dark shades under conditions which allow of strong oxidation by the air the dyebath may be improved by the addition of a little sodium sulphide. Dyeing is carried out for $\frac{3}{4}$–1 hour at 25–30° C. preferably under the surface of the liquor, and the dyeings finished in the usual manner recommended for the ordinary sulphur dyestuffs. Dyeings of Immedial Leuco Bordeaux R require to be soured with acetic acid to produce the true shade.

Miscellaneous Uses.—Mercerized cotton on being dyed with sulphur dyestuffs loses a good deal of its lustre. A subsequent after-treatment with a mixture of 3 parts good quality soap and 1 part olive oil emulsified with ammonia will be found to restore the lustre to some extent.

Linen, jute, hemp are dyed with sulphur dyestuffs on the same lines as cotton, though special care is required to see that the fibre is well penetrated. Sulphur black baths cannot be kept standing for the dyeing of jute owing to the lignin which comes out of the jute fouling the dyebath.

Section X.—THE AZOIC DYESTUFFS

The word " Azoic " is the distinguishing name given to those insoluble azo dyestuffs which are not applied directly as dyestuffs, but are actually produced within the fibre itself by impregnating the fibre with one component of the dyestuff followed by a passage through a diazo solution of the other component in an analogous manner to that employed in the manufacture of azo dyestuffs in substance. As ice is beneficial in preparing the diazo solution of the amines or diamines employed as the second component, this class of dyestuffs is also known as the " ice colours."

The idea of producing insoluble azo colouring matters in the fibre was first patented by Messrs. Thomas and Robert Holliday in 1880 (E.P. 2757), who padded cotton with an alkaline solution of B-naphthol and then coupled it with diazotized B-naphthylamine to produce a fine blue-red, Vacanceine Red, which was largely used in towellings. In the first patent the advantage of previously preparing the cotton with oil was not included, but this and other improvements were subsequently patented (E.P. 1638 of 1881 ; 2496 of 1882).

Holliday's process, improved by Weber, Galland, and von Gallois, and by Koechlin from 1887 to 1889, led to the issue of recipes for the production of Para Red on cotton by Meister, Lucius, and Bruning in 1889. Para Red, the most popular combination of this class of dyestuff, is a fine red produced by the coupling of B-naphthol and p-nitraniline and was first produced in substance by Meldola (*J.S.C.*, 1885, p. 662). This combination was particularly well received in Russia where Alsatian chemists played a prominent part in the development of this process in calico printing (in which it is most largely used) more especially in its application in discharge styles.

Other combinations with B-naphthol which have been used and the shades produced thereby are :

Paranitraniline	.. Red	p-Nitro-toluidine	..	.. Orange
a-Naphthylamine	.. Claret	Benzidine	..	.. Puce
B-Naphthylamine	.. Blue red	Tolidine	..	.. Puce
Metanitraniline	.. Orange	Nitrophenetidine	..	.. Pink

Dianisidine (with Copper salt) .. .. Blue

These dyestuffs give dyeings of good fastness to washing and chlorine, and have a light fastness superior to that of many direct cotton dyestuffs. With the exception of Dianisidine Blue coupled in presence of copper chloride they are also fast to acids. This class of dyestuff has two defects ; the first is that they rub off to a greater or lesser extent according to the skill with which they are dyed. This can be easily understood, since as the process consists of precipitating an insoluble dyestuff in the fibre, there is sure to be some precipitation on the surface. The degree of rubbing largely depends, therefore, upon the correct condition of the impregnating and coupling baths and the thoroughness with which the soaping is carried out. The second defect is that the dyestuffs sublime off the fibre on heating ; this is used as a characteristic test for this class of dyestuff, viz. : placing the pattern between white calico and ironing with a hot iron, when the dye-stuff will sublime on to the calico. This test does not apply to the shades produced from the Naphthol AS range, or to shades which have been coppered or coupled in the presence of a copper salt.

Para Red.—In the production of Para Red, which is typical of the method of application of these dyestuffs, the material is first padded with B-naphthol, dried, developed with diazotized p-nitraniline, washed, soaped, washed, and then dried.

The material to be dyed is first boiled out with alkali and then dried before being padded with a B-naphthol solution prepared by pasting $2\frac{1}{2}$ lb. of B-naphthol with $7\frac{1}{2}$ lb. Turkey Red Oil and $1\frac{1}{2}$ pints of 90° Tw. caustic soda and dissolving in 9 gallons of boiling water. Unless the material is evenly padded with the B-naphthol solution the resulting shade will be uneven when the Para Red is developed, so that the greatest care must be taken in wringing out the yarn or squeezing the pieces. Sticks used for yarn must be kept for this purpose only and should be saturated with the B-naphthol solution before being used. Usually 2 lb. of yarn are padded at a time and mechanically squeezed, fresh solution being added to the bath to replace the amount taken out by the yarn. The yarn is then dried on revolving drying machines or hung on sticks in the stove. Pieces are padded on a padding machine and dried in the hot flue, or less frequently, on drying cans. As B-naphthol sublimes at high temperatures drying

should be carried out at 50°–60° C. No more padding solution should be prepared than can be used in one day, since B-naphthol solutions tend to turn brown due to oxidation and so give flatter shades. This tendency to oxidation may be retarded by the addition of alkaline antimony oxide solution to the B-naphthol solution. For the same reason the dried padded material should be developed as quickly as possible. Again, the greatest care must be exercised in handling the dry padded material, as if it is touched with a wet hand, or a drop of water falls on it, there will be a yellow mark when the shade is developed, due to the dissolving-off of B-naphthol by the moisture.

The diazotization of p-nitraniline requires a certain amount of skill and practice, but if attention is paid to the following details a good result will be obtained. 2 lb. p-nitraniline are stirred into a paste with 3 gallons of boiling water, 5½ lb. of hydrochloric acid 32° Tw. added, and the mixture boiled until it clears. The solution must be clear or the subsequent diazotization will be unsatisfactory. 10 gallons of cold water are now added, with continuous stirring, so as to get a finely-divided precipitate of p-nitraniline hydrochloride. The suspension is allowed to cool and ice (if available) added to cool it to 3°–4° C. 1 lb. of sodium nitrite dissolved in 2 gallons of cold water is added, and the solution stirred until it clears—it is essential to add all the sodium nitrite at once. If the diazo solution does not clear on adding the nitrite, but a voluminous yellow precipitate is formed, this is a certain indication that there is a shortage of hydrochloric acid or sodium nitrite. Hydrochloric acid should always be present in excess, because it stabilizes the diazo solution, and sodium nitrite should also be present in excess to counterbalance any loss of nitrous fumes and to ensure that all the paranitraniline is diazotized. Both of these precautions prevent diazotized paranitraniline coupling with any unchanged paranitraniline present to form the voluminous yellow precipitate referred to above.
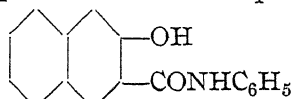
It will be gathered from the above that a method of avoiding the troublesome process of diazotizing paranitraniline would be desirable and a commercial success. Since 1894 stable diazotized paranitranilines in powder form have been on the market. The first stable form of diazotized paranitraniline manufactured commercially was Nitrosamine Red (G.P. 77874 of 1893) which was

put on the market in 1894. This is represented by the formula $NO_2C_6H_4N\begin{cases} NO \\ Na, \end{cases}$ and is formed by the addition of caustic soda

to diazotized paranitraniline until it is alkaline. Great hopes were built on this product in that it was thought possible to print the B-naphthol and Nitrosamine Red on the cotton together, and so produce Para Red in one process. Theoretically this was possible, but in practice it was not found possible to get good results. However, by an addition of hydrochloric acid to Nitrosamine Red diazotized paranitraniline is obtained, thereby providing a stable form of diazotized paranitraniline. Two other stable forms of diazotized paranitraniline were marketed as Nitrazol C, put on the market in 1897, and Azorphor Red PN (G.P. 85387 of 1894)—the latter consists of diazotized paranitraniline and desiccated Glauber's salt or aluminium sulphate. The azoic salt Fast Red 2G is also a stabilized form of paranitraniline. The use of these stable forms of diazotized paranitraniline is very convenient, as it abolishes the necessity for ice, which is not always obtainable, but it should always be remembered that they are more expensive.

The padded material is then passed through the cold solution of diazotized p-nitraniline when the Para Red develops practically instantaneously. No mineral acid must be present in the developing bath or coupling will not take place, and may be removed completely by the addition of sodium acetate, or since sodium acetate is expensive, part of the mineral acid may be neutralized with caustic soda or soda ash, the neutralization being completed with sodium acetate. The developing solution of diazotized paranitraniline (prepared as detailed above) therefore, requires to be diluted with 1 gallon of cold water, in which $1\frac{1}{4}$ oz. soda ash and $\frac{3}{4}$ oz. sodium acetate have been dissolved for every gallon of diazotized paranitraniline.

The Naphtol AS Dyestuffs.—The principle of producing insoluble dyestuffs on the fibre received a great extension when in 1912 the Chemische Fabrik Griesheim Elektron introduced a new naphthol which they called Naphtol AS. This compound is

the anilide of B-oxynaphthoic acid $\begin{array}{l} -OH \\ -CONHC_6H_5 \end{array}$

and was the first of a large series of similar compounds which have subsequently been developed. (A similar group of dyestuffs is now manufactured in this country, and marketed as the Brenthol dyestuffs.) The number of Naphtols now on the market is 25, and as there are some 44 different bases or Fast colour salts for use in conjunction with these Naphtols, 1,100 different dyestuffs can be produced on the fibre by this method. Included in the range of dyestuffs now possible with azoic dyestuffs are yellows, oranges, browns, scarlets, reds, maroons, blues, blacks, and one green, but this range, like all ranges of dyestuffs, includes combinations which are of little interest owing to their inferior shade or fastness properties, so that only a selected range has been adopted in practice. Despite the number of possible combinations it is surprising how many shades are asked for in practice which it is impossible to obtain with azoic combinations; this applies particularly to many furnishing shades, such as old rose tones. Another weakness of this group of dyestuffs is that there are no flattening agents, the blacks from Naphtols AS-SG and AS-SR being unsuitable for use in pale shades owing to their poor light fastness. In certain cases some flattening of shade may be achieved by mixing Naphtols giving the bluest and yellowest red shade with the same coupling component, e.g. by using Naphtol AS-LT (blue shade) and Naphtol AS-ITR (yellow shade) with Fast Red 3GL. Sometimes unexpected shades are produced by mixing Naphtols. Thus a mixture of Naphtol AS-LT and Naphtol AS-BG in equal proportions when coupled with Fast Red RL gives a shade on viscose rayon which is slightly yellower than the straight shade given with either Naphtol (see also Blakeley, *J.S.D.C.*, 1938, p. 454).

In choosing a suitable Naphtol consideration should be taken of the fastness required, of its substantivity and its price, whilst if it is necessary to mix Naphtols it is advisable to mix those having similar substantivities wherever this is possible. These dyestuffs are characterized by their beauty and brightness of shade, and in many cases by their all-round fastness. For example, Naphtol AS-BG coupled with Fast Scarlet GG gives a yellow-brown of excellent fastness to light, equal to that of the best vat dyestuffs; Naphtol AS-G coupled with Fast Yellow G

gives a yellow shade, and Naphtol AS–SW coupled with Fast Red KB gives a red shade, which are actually fast to pressure kier boiling, and subsequent bleaching ; while many combinations, such as Naphtol AS–ITR coupled with Fast Red ITR are fast to the same process of piece-bleaching as is used for bleaching fabrics containing vat-dyed effect threads. Some combinations possess a similar fastness to light, bleaching, etc., to that obtainable with the fastest vat dyestuffs, but the range is not large, and is particularly deficient in that there are no blues and green, whilst in pale shades the light fastness of most combinations is poor. Again, it should be noted that, with certain exceptions, these dyestuffs are not fast to peroxide bleaching, and that very few combinations will withstand the Trubenizing process due to their solubility in the solvent used.

The great advantage of the Naphtol AS group over B-naphthol is the substantive dyeing qualities of the various members which makes it permissible to omit drying the Naphtolated material, so that it may be passed straight into the developing bath after well squeezing it out of the Naphtol bath. Another difference is the addition of formaldehyde to the Naphtol bath which permits of the impregnated cotton being allowed to remain wet so that a large quantity of yarn may be prepared, then developed altogether instead of the usual 2 lb. at a time as with Para Red. Partial drying of the material must, of course, be avoided.

Like B-naphthol, these Naphtols are insoluble in water so that they also require to be dissolved in caustic soda and applied as their sodium salts, the amount of caustic soda used varying with the Naphtol used, for details of which the dyestuff makers' literature should be consulted. There are two methods for dissolving the Naphtols :

(a) *The Hot Dissolving Method.*—In this method the Naphtol is carefully pasted up with a dispersing agent (Turkey Red Oil) and the required amount of caustic soda ; boiling water is then added whilst stirring, and the mixture boiled under a steam pipe until a clear solution is obtained. With Naphtols AS–ITR, AS–SW, AS–BR, AS–GR, AS–SG, and AS–SR it is advisable to warm the pastes for a short time before adding the boiling water to achieve complete formation of the sodium salt. An alternative method which is preferred by some dyers is to paste the Naphtol

with Turkey Red Oil, add boiling water, boil under a steam-pipe, and whilst the mixture is boiling to add the caustic soda. This method is, of course, not suitable for dissolving those Naphtols which require to be warmed with the caustic soda before dissolving in boiling water. The clear solution of the Naphtol is then cooled to 120° F. (50° C.) by the addition of cold water, half the weight of Naphtol of 40 per cent. formaldehyde added where this is necessary, and after standing for 5–10 minutes the liquor is diluted to the required volume with cold water. Formaldehyde should not be added to Naphtol liquors which are to be used at high temperatures, since under these conditions there is a tendency for the Naphtol to precipitate. Complete solution of the Naphtol is absolutely necessary for impregnating the material as incompletely dissolved Naphtol will inevitably give faulty dyeings. With Naphtol AS–BR, AS–G, and AS–GR formaldehyde must not be added; this is particularly so with Naphtol AS–G as its dyeing power is destroyed by this addition. The value of the formaldehyde addition is that it retards the hydrolysis of the sodium compound to the free Naphtol, which normally has little coupling power so that weak and unlevel dyeings are obtained, and it also serves to protect the impregnated material from the effects of exposure to the air when not developed immediately (see Forster, Ramachandran, and Venkataraman, *J.S.D.C.*, 1938, p. 216). Addition of formaldehyde must not be regarded as eliminating the necessity for protecting the wet impregnated material as much as possible from the action of the air, and the material should be developed as soon as possible after removal from the Naphtol bath. With piece goods which are dried before coupling the formaldehyde may be omitted, as the impregnated material is only sensitive to air when in the moist state and is not readily affected when it has been quickly dried.

(b) *The Cold Dissolving Method.*—The Naphtol is stirred with the required amount of methylated spirit, the caustic soda, which is less than that required in the hot dissolving method, added; on the addition of cold water, a clear solution will be obtained. If formaldehyde is to be added it is added at this stage, the solution allowed to stand 5–10 minutes, and then poured into the dyebath set with Turkey Red Oil and the remaining caustic soda. The concentrated solution should not be left for

any length of time before adding to the dyebath as it is not very stable.

The hot dissolving method gives good results, but is more laborious than the cold dissolving method which gives more satisfactory results with the less soluble Naphtols. Again, the latter method enables more highly concentrated solutions to be obtained but it is, of course, rather more expensive, owing to the use of methylated spirit. A series of Naphtolates are also marketed which are very convenient to use. These consist of Naphtols containing the necessary amount of caustic soda for dissolving the Naphtol, together with a wetting agent, and are dissolved by the addition of boiling water; in other respects the method of working is the same as with Naphtols.

The Fast Colour bases for use with the Naphtols are diazotized by a similar method to that described for paranitraniline (p. 72), slight alterations in procedure being necessary depending on the actual base to be diazotized. For full diazotizing details the manufacturers' literature should be consulted. Thus with some bases, Fast Red TR base, the sodium nitrite is added to the solution or suspension of the base in presence of hydrochloric acid, whilst with others, Fast Red RL base, the base is pasted with the sodium nitrite and added to a dilute solution of hydrochloric acid. Sodium acetate is similarly added to the solution of the diazotized base in all cases excepting with Fast Red GL base, when sodium formate is recommended; with Fast Blue B base, when sodium bicarbonate is used; with Fast Blue BB base, Fast Blue RR base, and Variamine Blue B, where either zinc sulphate or zinc oxide is used. With several bases, Fast Yellow GC base, Fast Orange GC base, Fast Scarlet G base, Fast Red KB base, etc., an addition of acetic acid is also recommended. An undue excess of sodium acetate should be avoided as it has an unfavourable influence on the stability of the solution. For the same reason the sodium acetate should only be added immediately before the diazotized base is to be used. It is absolutely essential to see that the developing bath does not react acid to Congo paper, and the function of sodium acetate, zinc oxide, and sodium bicarbonate is to remove mineral acidity. After diazotizing and neutralizing, the diazo solution is filtered and poured into the cold dyebath containing

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20–50 gms. salt and 1–2 c.c. Diazopon A per litre. The addition of salt is unnecessary when developing dried goods, but is added when developing wet goods to prevent any Naphtol dissolving off the goods into the developing bath. Diazopon A, which was introduced in 1932, is added to the developing bath to give dyeings of improved fastness to rubbing by keeping any unfixed colour lake in colloidal solution and so preventing its deposition on the fibre. The stability of the developing bath during the developing process is increased by the addition of what are known as " alkali binding agents." These are substances such as aluminium sulphate, zinc sulphate, and acetic acid, which neutralize the caustic soda brought into the developing bath by the Naphtol impregnated material, and so prevent the bath from becoming alkaline. The use. of such substances is essential because if the developing bath becomes alkaline it soon becomes ineffective. There is no general rule regarding the use of alkali binding agents, but with some exceptions an addition of acetic acid is the agent most commonly used. Solutions of the diazotized bases vary considerably in their stability on keeping, but are dependent to a large extent upon the care devoted to the diazotization process, and on the temperature and acidity of the solution. The stability is increased by the addition of Diazopon A which has the added advantage that it keeps in solution any decomposition products which may be formed. Particular care should be taken to avoid the accidental heating of the diazo liquor by leaking steampipes which will produce a poor result, the cause of which may not be readily recognized.

As the diazotization of many of the bases presents difficulties to the inexperienced, and in order to simplify the process the makers supply Fast Colour salts which consist of the stabilized diazo-salts of the corresponding Fast Colour bases, the stability being produced by coupling the diazotized bases with naphthalene sulphonic acids or fluorosulphonic acids (see Dorman, *Amer. Dyestuff Rep.*, 1939, p. 104). These Fast Colour salts render the always tiresome operation of diazotization unnecessary, and are of great convenience in practice on account of their regular composition, excellent stability, and good solubility. They are generally neutral to Congo Red paper so that the addition of sodium acetate is unnecessary, and in the majority of cases contain

sufficient alkali binding agent to meet normal dyeing conditions. There are, however, a few exceptions ; thus an addition of acetic acid is made to combinations of Fast Colour salts with Naphtol AS-G and always to Fast Red Salt ITR, Fast Red Salt KB, and Fast Red Salt RL, whilst Fast Scarlet G requires to be neutralized with sodium acetate. The developing baths are prepared by pasting the Fast Colour salts with about 5 times the weight of lukewarm water, dissolving in cold water, and sieving into the bath when a clear solution is obtained. They are little more expensive than the bases, but as they are less wasteful they are probably as cheap ultimately unless large runs of one combination are concerned. In dyehouses where continuous runs of one combination are not usual, but odd lots of different combinations, then the Fast Colour salts are almost indispensable.

Further work on the application of the azoic dyestuffs led to the introduction of the Rapid Fast, Rapidogen, and Rapidazol dyestuffs, which are widely used in calico printing, but not for producing solid shades, which may be obtained more cheaply by the impregnation process with the necessary Naphtol and Fast Colour base or salt. The Rapid Fast dyestuffs, which were patented in 1914 by the Griesheim Elektron and announced in 1916, consist of the alkali metal salts of the nitrosamine of the base mixed with the sodium salt of the Naphtol. The early Rapid Fast dyestuffs were not very stable, and being pastes they dried up rather rapidly in storage ; they may now be obtained in powder form. These dyestuffs are pale yellow in colour and dissolve easily in cold water to give solutions which when warmed or acidified precipitate the azoic dyestuff ; the presence of alkali or sodium chromate increases their stability. As the nitrosamines of certain bases are either unstable or insoluble other means of producing stable mixtures of diazo-compounds and Naphtols were sought. This led to the introduction of the Rapidogen dyestuffs which consist of mixtures of the sodium salt of the Naphtol with diazoamino compounds of amino acids *e.g.* sarcosine. On acidifying this mixture the free diazo compound is liberated, and coupling can then take place. More recently the Rapidazol dyestuffs have been developed. In producing these dyestuffs the diazo compound is converted into an alkaline salt of a diazo-sulphonic acid or

hydrazine sulphonic acid, and mixed with the alkaline salt of the Naphtol. The development of these dyestuffs can only be brought about by steaming in the rapid ager, and not by a simple treatment with acids (see Desai, Mehta, and Thorar, *J.S.D.C.*, 1938, p. 371).

Cotton.—Cotton may be dyed with the azoic dyestuffs in all its various stages of manufacture, although by far the greatest proportion is dyed either in the skein, warp or piece form. Skeins may be dyed either in the open beck, in a liquoring machine, such as the Spencer padding machine, or in machines on the pack system, the choice of method depending on the quantity of yarn to be dyed and on the available equipment. Warps may be dyed in the ordinary warp dyeing machine, taking care to give an efficient nip to the naphtolated material before passing it into the developing bath. Alternatively they may be dyed in a pack dyeing machine of the " Obermaier " type. With the latter, it is advantageous if the " Obermaier " cage can be removed from the liquor and hydro-extracted. For pieces, the padding machine with a double nip is the ideal method for their application, although the jigger can also be used if followed by an efficient squeeze on the mangle. In many cases it is found advisable to dry warps and pieces after impregnation with the Naphtol in order to give a better rubbing fastness; drying may be carried out either in a hot-flue or on a cylinder drying machine, care being taken that the cylinders are not excessively heated. In all cases, the method of application of these dyestuffs is first to impregnate with the Naphtol solution, remove excess of liquor from the material, and then to develop in a solution of either a diazotized base or a Fast Colour salt. In calculating the quantities of Naphtol and base or Fast Colour salt required it is customary, on cotton, to calculate the quantities in grams per litre in order to simplify calculation of the quantities of feeding liquor required, but with viscose rayon, which does not require the use of feeding liquors, and is usually not required in bulk runs of one shade, the authors recommend the calculation of quantities as a percentage on the weight of rayon to be dyed. Although the Naphtols are absorbed substantively by cotton the substantivity of the individual members varies considerably; with the less substantive Naphtols, as Naphtol AS and Naphtol AS–D, about 10–20

per cent. Naphtol is absorbed, whilst with the highly substantive Naphtols, as Naphtol AS–SG, AS–SR, and AS–GR, the baths are practically completely exhausted. On economical grounds it is, therefore, advisable with the less substantive Naphtols to use continuous baths and to replace the Naphtol taken from the bath by feeding liquor. The amount of feeding liquor used depends upon the conditions of impregnation, and for guidance on this point the reader is referred to the dyestuff manufacturers' literature. It can, however, be said that a short liquor ratio favours exhaustion of the bath and that, with the exception of Naphtol AS–BR, the affinity of the Naphtol is greater cold and is reduced at high temperatures, so that in order to get better penetration of tightly twisted yarns or tightly woven fabrics impregnation should be carried out at high temperatures. With the less substantive Naphtols an addition of common salt favours their exhaustion. As the developing baths are not usually exhausted by being used once, they are, like the Naphtol baths, kept up to strength by feeding liquors.

After the dyeings have been developed, the diazo solution still adhering to the material must be removed by rinsing with cold water [when the developing bath contains aluminium sulphate the use of a mildly acid rinse is to be recommended], and the material soaped as hot as possible with soap and soda. This after-soaping must be very thorough as it serves to develop the true shade of the combination used, to increase the fastness to rubbing by removing loose pigment adhering to the surface of the material, and to increase the fastness of the dyeing, particularly to chlorine and light (see Bean and Rowe, *J.S.D.C.*, 1929, p. 67). With combinations which show a tendency to rub steeping overnight in a 1 per cent. soap solution may be used. The material is entered into the boiling soap solution and allowed to cool overnight. Although this method, apart from its cost, may have certain objections in practice it deserves serious consideration. The authors have obtained excellent results on yarn by steeping overnight in hot soap solution of this strength, washing in hot water, and then giving a normal soaping with 5 per cent. soap (on the weight of yarn) to remove any dirty soap liquor and loose pigment left in the yarn.

The most satisfactory method for obtaining fastness to rubbing

on hanks is, however, to soap on machines similar to the combined scouring and rinsing machine made by Edward Simpson & Co., Ltd., of Glasgow (see " Textile Manufacturer," September, 1933) which alternatively saturates with liquor and squeezes the hanks. This method cannot be used with rayon, which would be damaged by the squeezing.

Viscose Rayon.—This group of dyestuffs finds a definite sphere of usefulness on viscose rayon yarns in the dyeing of shades which are required to be fast to light, boiling, washing, bleaching, and cross-dyeing. The general method for their application is similar to that employed for cotton, but acetic acid, not aluminium sulphate, should be used as the alkali binding agent to prevent precipitation of aluminium hydrates in the dyebath, which would result in dulling of the lustre of the rayon. Again, it is obvious that the padding and wringing process employed for cotton yarns cannot be used for rayon skeins owing to the mechanical damage which would result. Advantage is, therefore, taken of the superior substantivity of the rayon to that of cotton for the Naphtol which makes possible the economical application of the Naphtol from a salt bath. Common salt should also be added to the developing baths to prevent the bleeding of Naphtol from the yarn to the developing liquor during this process, which if allowed to occur would result in the production of unlevel and dirty dyeings. This method has the further advantage that it dispenses with any elaborate calculations as to the feeding of the bath, because the batch of yarn, particularly when using the roller type of machine, is dyed to the same shade owing to the whole of the batch being impregnated simultaneously with the Naphtol solution in the same bath. It has been proposed to hydro-extract the rayon after impregnating with the Naphtol, but this requires very special precautions in order to avoid white marks caused by the handling necessary during the wrapping of the yarn into cloths and the loading and unloading of the hydro-extractor. Again, as the hydro-extractor has yet to be built which will extract evenly the liquor from a batch of rayon skeins this method is not recommended by the authors.

No difficulties arise in dyeing the azoic dyestuffs on viscose rayon, providing the coupling is very rapid, but with slow-coupling combinations the insides of the skeins are liable to be

almost undyed. On the roller type of machine this difficulty can be minimized by hand turning the yarn whilst the rollers are rotating so as to open out the yarn and allow the developing solution to come rapidly into contact with all parts of the Naphtolated skeins.

The shades produced by the azoic dyestuffs on viscose rayon are much superior in fastness to rubbing in comparison with the same shades on cotton, more especially on single yarns. Multiple twist yarns, however, are not so satisfactory owing to the presence of particles of solid colouring matter held in the interstices of the twist which are difficult to remove even on prolonged or steep soaping. Although azoic dyeings may be soaped until the soap liquor is perfectly clear such dyeings are very susceptible to marking-off under pressure.

One of the defects of the azoic dyestuffs, against which precautions have to be taken, is the liability of certain combinations to blind the rayon on treatment with boiling soap. Rowe, (*J.S.D.C.*, 1926, p. 208), has examined and explained this phenomenon with the aid of microphotographs. Thus he states that " the lustrous non-blinded fibres consist of a true solution of the colour matter in hydrated cellulose, whereas the blinded fibres consist of a suspension of microcrystalline aggregates of the colouring matter which are evenly disseminated throughout the colourless fibres. The coagulation or crystallization of the colouring matter within the fibres is solely a temperature effect, and the blinded fibres are actually as lustrous as the non-blinded, but the particles of solid colouring matter in the former mask the lustre " (Reinthaler-Rowe, " Artificial Silk," p. 196). Those Naphtols and bases which are known to be liable to produce this blinding effect must therefore be carefully avoided, but as the choice of possible combinations is so wide, this does not seriously limit the range of shades which can be produced on viscose rayon.

Acetate Rayon.—As the Acetate " Dispersion " dyestuffs are not sufficiently fast for shades fast to boiling and degumming, the natural sequence was to investigate possible methods for applying the vat and azoic dyestuffs to cellulose acetate rayon. These dyestuffs can be applied to cellulose acetate rayon which has been previously saponified (Sect. XIII) but the method is not

to be recommended for the azoic dyestuffs, as more recent work has shown that they can be satisfactorily applied to the unsaponified rayon, thereby avoiding all the disadvantages of saponification.

When dyeing the azoic dyestuffs on cellulose material, the Naphtol is applied to the cellulose and then coupled with a diazotized base in a second bath, but when this method is used with unsaponified cellulose acetate rayon, the rayon is only stained to an extent depending upon the Naphtol and based used. Similar results are also obtained by treating the rayon with a diazotized base followed by treatment with the Naphtol. If, however, the Naphtol and base are applied to the rayon in the same dyebath full azoic shades may be obtained by treating the rayon in a diazotizing bath (*Silk Journal*, Feb., 1935, pp. 26, 36 ; Pokorny, *J.S.D.C.*, 1926, pp. 345–348 ; Metzger and Rohling, *Textilberichte*, 1937, p. 644 ; Rohling, *ibid.*, 1939, p. 63). The following method has been found to give good results in practice. The Naphtol is dissolved by pasting with an equal weight of soluble oil, and then adding an equal weight of 70° Tw. caustic soda, and carefully diluting with boiling water. The base is pasted with 3 times its weight of soluble oil, and diluted with hot or cold water depending upon the base used. After mixing the solutions in the dyebath, acetic acid is added till the solution reacts faintly alkaline to litmus. Dyeing is carried out at 80° C. for $\frac{1}{2}$–1 hour, and the shade is developed cold, using 6 per cent. sodium nitrite and 10–16 per cent. hydrochloric acid for $\frac{1}{2}$ hour. The dyeing is washed in cold water, then in hot water to remove excess of Naphtol or base, and finally soaped at a temperature suitable to the dull or bright finish desired.

The proportion of Naphtol to base depends on their relative affinity for cellulose acetate rayon, so that it is not possible to give general proportions, and each individual combination requires investigation on this point. Thus with Naphtol AS–SW and Fast Garnet G base a proportion of 3 to 1 is the best, whilst with Naphtol AS–OL, and Fast Scarlet R Base the best proportion is 3 to 2.

Silk.—Combinations of the Naphtol AS series are employed to a small extent on silk yarn, and give shades of excellent fastness to light, washing, and even, degumming ; but they are not

always fast to rubbing. It is a curious fact that the number of Naphtol combinations of satisfactory fastness to degumming is relatively limited, especially as many combinations are fast to boiling soap and soda when dyed on cotton. The degree of fastness to degumming required is high, as it is absolutely essential that adjacent white or light shades are free from tinting after this process.

Impregnation of silk with the Naphtol is done in a similar way to that used for cotton, but as the Naphtols have a poor affinity for silk, stronger baths, larger additions of salt, and a longer time of impregnation are necessary in order to keep down the cost of dark shades. The injurious action of caustic soda on silk is well known so that it is necessary to control the alkalinity of the Naphtol baths; for light shades the amount of caustic soda used is approximately the same as for cotton, but the amount is reduced for heavy shades, whilst protective colloids may also be added for this purpose. Everest and Wallwork's method for the application of these dyestuffs to wool can also be used (see under " Wool ").

It has been known for a long time that diazo compounds have a strong affinity for silk so that when coupling takes place the diazo-compound combines partly with the Naphtol and partly with the silk, giving yellower shades than are produced with the same combination on cotton ; addition of acetic acid to the ordinary coupling bath minimizes this effect.

After development it is advisable to sour the material with dilute hydrochloric acid, and, after rinsing with water, to soap the material twice at as high a temperature as possible.

Wool.—Most of the remarks on the application of the azoic dyestuffs to silk apply with equal force to wool, but as far as the authors are aware these dyestuffs find little application on this fibre.

Work on this subject has been carried out by Everest and Wallwork (*J.S.D.C.*, 1928, p. 101 ; 1929, p. 235 ; 1934, p. 37) who found that it is possible to apply the Naphtols from a soap and soda ash bath without the use of caustic soda, since the Naphtols show a decided substantivity for wool. Briefly, the method is to dissolve the soap and soda in boiling water, add the Naphtol which has been made into a smooth paste with a little

soap solution, sieve, boil 5 minutes, and make up to volume with cold water. The yarn is then entered at 50° C. worked 20–30 minutes, whizzed, developed for 30 minutes, and finished by rinsing with water, followed by dilute acetic acid, whizzing and drying.

Section XI.—THE VAT DYESTUFFS

ALTHOUGH the vat dyestuffs may be classified into three chemical groups, viz. :

Anthraquinone dyestuffs ... Caledon Jade Green (C.I. 1101).
Indigoid dyestuffs ... ... Ciba Blue 2B (C.I. 1184).
Sulphide dyestuffs ... ... Hydron Blue G (C.I. 971).

they are all similar to the dyer in that they are insoluble in water, only passing into solution when they are reduced to their leuco compounds which are readily soluble in alkali. They are applied to fibres in the latter form, the dyestuff being regenerated and precipitated in the fibre by oxidation.

This class of dyestuffs, with the exception of Woad and Indigo, is amongst the most recent to be produced commercially, the first member, Indanthren, being discovered by René Bohn and put on the market by the Badische Company in 1901. After Indigo, the first of the Indigoid dyestuffs to be synthesized was Thioindigo Red, which was discovered by Friedländer in 1905, whilst in 1909 Hydron Blue was discovered by Hertz. Though these dyestuffs include some of the fastest dyestuffs known, it is necessary to emphasize that a vat dyestuff, because it is a vat dyestuff, must not be assumed to be fast. Indeed some vat dyestuffs have poor fastness properties. In general, the Anthraquinone dyestuffs include the fastest types, followed by the Sulphide dyestuffs, whilst the Indigoid dyestuffs are the least fast ; conversely, the Indigoid dyestuffs do not present the same applicational difficulties as do the Sulphide and Anthraquinone dyestuffs.

The vat dyestuffs were not, however, readily adopted by the dyeing trade because their application was unusual, difficult and expensive, and it required a long period of educational propaganda by the dyestuff manufacturers together with prolonged trials by master dyers before they were widely adopted by the trade. The buying public has, however, been so educated by leading

textile firms to demand guaranteed articles, particularly in furnishing and washing fabrics, that dyers have been increasingly compelled to use them. On the large scale the vat dyestuffs are very difficult to apply, requiring expert attention and manipulation in order to get satisfactory results. Although the dyeing trade has made great strides in overcoming these difficulties it must be admitted that there is still room for considerable improvement. Exact matching to pattern cannot always be given unless topping with direct cotton dyestuffs is permissible, whilst lack of penetration is still one of the defects which the trade has not completely overcome. This latter defect is due to the great affinity of the leuco compound of the dyestuff for the fibre ; individual dyestuffs vary considerably in this respect, but it will usually be found that the fastest dyestuffs have the greatest affinity.

It was only to be expected that dyestuff manufacturers would endeavour to market vat dyestuffs in a soluble form with the double object of making their application easier and expanding their use on animal fibres by avoiding the use of alkali. This object was obtained in 1922 when Bader and Sunder in association with Durand, Huguenin & Co. patented a method (E.P. 186057) for making Indigo and Indigoid vat dyestuffs soluble in water without the necessity of vatting in alkaline solutions, the products being stable in air and applicable to both vegetable and animal fibres. A similar range of dyestuffs is manufactured by I.C.I. (Dyestuffs Group) from Anthraquinone vat dyestuffs, and sold as the Soledon dyestuffs. Although the solubilized vat dyestuffs are necessarily more expensive than the parent vat dyestuff it is the authors' opinion that when the range has been further extended, these dyestuffs will eventually supplant the vat dyestuffs for certain types of work owing to their ease of application and to the excellent results obtainable in practice. Oxidation difficulties are much less compared with dyeing from an alkaline vat ; the affinity is also more under control.

From a survey of the dyeing properties of the vat dyestuffs, Boulton and Morton (*J.S.D.C.*, 1939, p. 481) conclude that the mechanism of absorption by cellulose of the leuco-vat dyestuffs is fundamentally similar to that of the direct cotton dyestuffs. The diffusion speeds of the alkaline leuco-vat dyestuffs are, on the whole, much smaller than those of the direct dyestuffs, possibly

because of the lower temperature of dyeing, and their greater substantivity.

<div align="center">INDIGO</div>

Indigo, which is one of the most important representatives of the vat dyestuffs, is probably the oldest dyestuff known to man, and is firmly established in the estimation of the public as synonymous with fastness. Formerly, Indigo was solely obtained from the Indigo plant, but in 1897 synthetic Indigo was marketed as Indigo Pure BASF, an event which was a great chemical achievement and has had the effect of almost completely replacing the natural product. As a natural sequence the manufacture of synthetic Indigo was followed by the production of the various halogenated Indigos, such as Ciba Blue 2B.

Indigo is dyed on cotton and wool, and to a limited extent, on silk. Two general methods are employed for producing an Indigo vat :

1. Reduction by fermentation.
2. Reduction by chemical agents.

The chemical principles involved in both of these methods are . simple. Indigo, which is insoluble in water, combines on reduction with two atoms of hydrogen to form a colourless leuco compound, Indigo white, which reacts as a weak acid and whose alkali salts are soluble in water. It is, therefore, necessary for an Indigo vat to be alkaline in order to have the Indigo white in solution, and in a condition capable of being absorbed by the fibre. The fastness and beauty of the shade are largely governed by the condition of the vat. For example, if the vat is short of alkali the shade produced is redder. Shortage of alkali also results in poor pentration and poor fastness to rubbing because the Indigo white is insufficiently dissolved by the alkali available and particles are deposited on the surface of the material. The practical application of Indigo necessitates a long experience of large-scale working in order to become efficient. For the following details of the various vats Badische's book on Indigo and the I.C.I. booklet " Indigo LL on wool " have been largely used.

Wool.—Wool is chiefly dyed with Indigo in piece form and to a less extent as loose wool and slubbing. In whatever form it is dyed it is absolutely essential that it should be perfectly free from

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Wool.—Wool is chiefly dyed with Indigo in piece form and to a less extent as loose wool and slubbing. In whatever form it is dyed it is absolutely essential that it should be perfectly free from

grease, or poor results, particularly as regards fastness to rubbing, are sure to be obtained. Again carbonized wool must be thoroughly neutralized with soda ash before it is dyed, since any acid on the wool will tend to upset the condition of the vat by neutralizing the alkali. The wool should be wet when entered into the vat, since dry material takes in too much air which would disturb the condition of the vat.

Indigo is dyed on wool either in the fermentation vat, or, more generally, in some form of hydrosulphite vat. In both vats the controlling factor is alkali. If excess of alkali is present the wool may easily be damaged, in addition to which excess alkali prevents the wool from absorbing the Indigo white, thus making the dyeing of dark shades difficult. A shortage of alkali reflects itself in the poor condition of the vat owing to the Indigo white not being in good solution, thus giving dyeings which scour and rub badly owing to Indigo being deposited on the surface of the fibres.

The Fermentation Vat.—This vat is probably the oldest known dyeing process and, although it is seldom used in this country, is still fairly widely used in the East. The disadvantages of the fermentation vat are that it cannot be worked until 3 days after it has been set, it is difficult to control, and there is a loss of Indigo due to over-reduction, particularly after it has been used for some time.

The fermentation vat most commonly used in Great Britain was the Woad vat, which, to avoid loss of Indigo, required much practical experience and attention to keep it in good condition. Such a vat may be worked for 9 months before it is necessary to exhaust it and run it off.

The following recipe is for a dark blue, though it may naturally be varied within wide limits, owing to the nature of the vat :

Capacity of vat	..	..	..	..	2,500 gallons.
Indigo, 20 per cent paste		..	..	60 lb.
Woad	..	..	..	..	500 ,,
Bran	..	..	..	..	30 ,,
Madder	..	..	..	..	10 ,,
Lime	..	..	..	..	12 ,,

The water is heated to 60° C., the crushed woad added, and this is stirred at intervals until thoroughly soaked, or it is left overnight. The Indigo, Madder, bran, and lime are added and thoroughly stirred, after which the vat is covered over to prevent

loss of heat and access of air, until fermentation sets in. This takes place in 12-16 hours. When fermentation sets in the bluish-red colour changes to green, and the vat smells sweet. The vat is well stirred, and slaked lime is added in small quantities at intervals, until the liquor changes from green to yellow, with a bronzy scum, termed flurry, and the sweet smell changes to a sharp one. The vat will be ready for dyeing in 2 to 3 days from commencing to set it. When it appears to be ready it is tested by dyeing in it a small quantity of wool. This should appear greenish-yellow on taking out of the vat, and should slowly turn blue on exposure to the air. On being scoured it should not lose much colour. Until the vat has become seasoned, too much wool must not be worked through it. When it is in proper condition the vat is stirred up first thing in the morning, and sharpened with lime. After the sediment has settled dyeing proceeds for 2-3 hours, when it is again stirred up, sharpened, allowed to settle, and dyeing continued for a further 2-3 hours. Dyeing is then stopped for the day, and the vat is heated up to 50° C. Indigo, woad, and bran are then added, the fermentation regulated by addition of lime and the vat covered up for the night. Next morning the vat is stirred up, lime added if necessary, and the above procedure repeated.

The temperature of the vat should not be allowed to fall below 45° C., otherwise the fermentation may become too sluggish. Too active fermentation may be regulated by the addition of lime, whilst too sluggish fermentation is accelerated by the addition of bran ; an excess of lime produces duller shades of blue. On the Continent the soda fermentation vat is preferred to the woad vat ; treacle is used in place of woad, and soda in place of lime.

The Hydrosulphite Vat.—This vat was patented in 1871 by Schützenberger and De Lalande, the British rights being bought by Read Holliday & Sons, Ltd. At this time the hydrosulphite had to be made by the addition of zinc dust to sodium bisulphite so that the vats gradually accumulated a sediment ; sodium hydrosulphite was not then commercially available. The alkali first recommended was lime and was later followed by caustic soda which has the advantage of reducing the quantity of sediment in the vat. With the production of sodium hydrosulphite in stable powder form by the Badische Company the ease of working

was further facilitated, and a vat free from sediment was obtained, in which no Indigo was lost, and which could be successfully used in machine dyeing. Ammonia has been added to the alkalies used for dissolving the Indigo white, so that using this alkali or caustic soda, vats may now be obtained perfectly free from sediment, thus allowing the size of the vats to be reduced considerably. The hydrosulphite vat is a chemical vat in which the action of each ingredient is definitely understood, so that it is under closer control than is possible with a fermentation vat, nor does it require the same personal attention. The absence of sediment also enables the vat to be set and used the same day, which avoids all loss of time waiting for the sediment to settle, so that the possible production from the vat is much greater.

Unlike the fermentation vat, the Indigo is not reduced in the actual working vat, but a concentrated stock vat is made from which definite quantities of ready reduced Indigo may be measured to replenish the working vat.

The Bisulphite Zinc-Lime Vat.—From the constituents of this vat it follows that large amounts of sediment are formed so that one of the disadvantages of the fermentation vat is still present. This sediment has a detrimental effect on the handle of the wool since the accumulated zinc salts, unless allowed to settle completely, have a definite tendering effect and at the same time tend to produce spotty dyeings as a result of their resist effect. Again owing to the presence of zinc in the vat there is always a certain loss of Indigo. The stock vat is prepared by intimately mixing in a cask.

20 lb. Indigo 20 per cent. paste.
1 gallon hot water.
2 gallons milk of lime, 20 per cent.

A mixture of zinc and sodium bisulphite is then prepared by gradually adding $2\frac{1}{2}$ lb. of zinc dust to $2\frac{1}{2}$ gallons of sodium bisulphite 57° Tw. and allowing to stand until free from the characteristic smell of sulphur dioxide : if the smell does not completely disappear more zinc must be added. This process is termed " killing " the bisulphite. The zinc bisulphite is then added to the Indigo and lime mixture, the whole well stirred and diluted with $12\frac{1}{2}$ gallons of water at 65° C., covered over and

allowed to stand for 2 hours or better still overnight. In setting the vat the water is heated to 50° C., " killed " bisulphite added to remove dissolved oxygen in the water, followed by the requisite amount of the stock vat. It is then stirred, allowed to settle, and dyeing carried out in the normal way.

When in proper condition the vat should be greenish-yellow ; a green or blue-green colour indicates that the vat is short of " killed " bisulphite, whilst a bright yellow colour shows the presence of too much alkali. The vat should not be worked longer than 3 weeks before it is exhausted and run off. Owing to the presence of lime, wool dyed in this vat must be soured with HCl before washing to prevent it having a harsh handle.

The Hydrosulphite-Soda Vat.—This vat is in principle the same. as the bisulphite zinc-lime vat, excepting that caustic soda is used as the alkali and sodium hydrosulphite powder as the reducing agent. It must be recognized that with the hydrosulphite-soda vat careful supervision is essential, since even a small excess of caustic soda will have a very detrimental effect on the wool.

A stock vat is prepared by stirring 15 lb. Indigo 20 per cent paste in 3 gallons of hot water, adding 3 pints caustic soda 77° Tw., and reducing at 60° C. by the gradual addition of 3 lb. sodium hydrosulphite powder. The working vat is set by heating the water to 50° C. removing dissolved oxygen in the water by the addition of ammonia and hydrosulphite powder (1 quart ammonia, 17 per cent. to 5 oz. hydrosulphite powder), adding glue solution as recommended for the hydrosulphite ammonia vat (see below), and finally the requisite amount of the stock vat.

The Hydrosulphite-Ammonia Vat.—Ammonia itself is almost incapable of dissolving Indigo white, but it was discovered by Meister, Lucius, and Brüning that Indigo white is not precipitated in the presence of glue and ammonia, but assumes a colloidal form, which possesses a great affinity for the fibre. For use in this vat a specially reduced Indigo is marketed, consisting of Indigo white plus ammonia and a minimum quantity of fixed alkali. The dyer is, therefore, saved all the trouble of reducing the Indigo and simply measures a given quantity out of the cask. The commercial names of this form of Indigo are Indigo MLB vat 1, Indigo solution BASF 20 per cent., and Indigo LL. vat 1.

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A working vat is set as follows : For a vat of 600 gallons the water is heated to 50° C., $1\frac{1}{2}$–3 pints ammonia (17 per cent.), 2 gallons glue solution (10 per cent.), 2–4 gallons of the special Indigo solution and $2\frac{1}{2}$–5 lb. hydrosulphite powder added in this order. After well stirring the vat should be a clear greenish-yellow colour, and the wool when it is taken out of the vat should be pale green in colour. The vat should not be run longer than a week, and 2 quarts of glue solution (10 per cent.) should be added twice during this period.

Dyeing Methods.—Piece goods are usually dyed with Indigo in the hydrosulphite-ammonia vat, but for heavily milled cloths the fermentation vat is still used owing to the superior penetration obtained as compared with the hydrosulphite vats. Dyeing is generally done in the hawking machine which consists of two mechanically driven squeezing rollers fitted with openers so as to avoid folds of cloth passing through the rollers. The average duration of a dip varies from 20–45 minutes, but pieces which are difficult to penetrate may be kept in the vat for 1–2 hours. For pure Indigos the more dips which are given the better is the wool dyed, thus a shade dyed in two dips will be faster to rubbing than the same shade dyed in one dip. When the pieces are taken out of the vat they are immediately passed through overhead squeezing rollers which may be run on an overhead rail from vat to vat as required. Unless these squeezing rollers are free from defects uneven pieces will result. After the pieces have been thoroughly oxidized and washed on the dolly they are treated with Fuller's earth or soap in order to remove all superficially attached dyestuff which would otherwise cause the shade to rub, and finally well washed in water. If the shade has been dyed from a vat out of condition no amount of after-treatment will make it fast to rubbing.

Slubbing can be dyed in hank form in open dyebaths. The material should be completely immersed during dyeing, and on removal from the dyebath run through squeezing rollers as soon as possible. In some cases slubbing is dyed in a continuous form by passing it through the vat in the form of a band over a series of rollers situated alternately near the top and bottom of the vat. The best results, however, are obtained by dyeing in the top form in circulating machines of the Obermaier or Longclose types, using

the hydrosulphite ammonia vat, followed by immediate hydro-extraction to remove surplus dyeliquor.

Loose wool is often dyed in circular cast-iron vats, which are so sunk in the ground that they project about $2\frac{1}{2}$ ft. above the ground. They are usually built round with bricks and fitted with a steam coil for heating purposes. Before dyeing is commenced a trammel net is inserted in the vat and arranged at such a height that it keeps the wool clear of the sediment. When the wool is due out, a pair of squeezing rollers on wheels is brought to the side of the vat, which has a travelling apron so fitted that it projects over the side of the vat, underneath which a tray is fitted so as to return all the surplus liquor to the vat. The wool is lifted on to the apron by means of sticks or forks, and after passing through the nip rollers it falls on the floor where it is allowed to lie in heaps till oxidized. Loose wool can also be dyed in circulating machines.

Indigo may be topped with a variety of dyestuffs to produce " woaded " shades. Thus woaded blacks are produced by dyeing logwood on top of Indigo, whilst woaded greens are produced by combining fustic with the logwood. When chroming on top of the Indigo great care must be taken to avoid destroying the Indigo, which is sensitive to oxidizing agents.

Cotton.—Cotton may be dyed with Indigo at all stages of manufacture, but is seldom dyed as loose cotton. In whatever form cotton is dyed it is absolutely essential that it be thoroughly boiled out with alkali before dyeing in order to obtain the best results. Indigo on cotton is not as fast as it is on wool, nor is it as fast as the more recently developed vat blues. Compared with the sulphur blues, which usually wash redder, it has the advantage that despite loss of depth it retains its tone.

There were formerly three principal vats used for dyeing Indigo on cotton, viz. :

1. Copperas vat.
2. Zinc-Lime vat.
3. Hydrosulphite vat.

but the copperas vat has gradually fallen out of use owing to the very bulky sediment produced, which is 5 times bulkier than that of the zinc-lime vat, whilst the loss of Indigo is much greater than in the case of the other two vats. The hydrosulphite vat is the most advantageous, due to its freedom from sediment and

ease of control, and is largely used, particularly since the widespread adoption of machine dyeing.

Zinc-Lime Vat.—In the formation of this vat the lime and zinc dust react to form calcium zincate, whilst the hydrogen liberated produces the Indigo white, which then dissolves in the excess of lime present : $Zn + Ca(OH)_2 = CaZnO_2 + H_2$.

In preparing the stock vat 20 lb. Indigo, 20 per cent. paste, and $2\frac{1}{2}$ lb. zinc dust, made into a paste with 4 gallons of water at 60° C. are mixed together, 8–10 lb. quicklime made into a smooth paste is added, the whole is made up to 20 gallons with water at 60° C., and well stirred at intervals. The mixture will reduce to a clear yellow. Before adding to the working vat, the water is sharpened with 1 oz. zinc dust and $1\frac{1}{2}$ oz. lime for every 10 gallons.

Hydrosulphite Vat.—This vat has gradually replaced the older vats in the application of Indigo to cotton, and is used for the dyeing of all forms of cotton. The stock vat is made up as follows :

100 lb. Indigo, 20 per cent. paste, is intimately mixed with 6 gallons caustic soda, 76° Tw., 20 gallons water, 17 lb. hydrosulphite powder conc. added, and the whole warmed to 45° C. The Indigo should be reduced and ready for use in half an hour, when the liquor should be a clear yellow ; if the liquor appears green and oxidizes too quickly more hydrosulphite should be added. Before adding the stock vat to the working vat the water is sharpened with 1 oz. hydrosulphite powder conc. for every 100 gallons water. The working vat should be yellow to greenish-yellow in appearance, and if it loses this appearance it should be brought back into condition by addition of a little hydrosulphite and caustic soda.

Yarn is principally dyed by hand with a mechanical squeezing arrangement fitted over the top of the vat to ensure that all hanks are submitted to the same degree of squeezing and so give the same depth of shade. As a rule about 2–$2\frac{1}{2}$ lb. is suspended on each of three sticks and turned alternatively for 5–10 minutes in the cold vat. As soon as one stick load has been squeezed another stick is entered into the vat so that there is always three sticks being treated alternately. After squeezing the yarn is wrung, shaken out on a peg, hung to oxidize, and washed off. The number of dips given depends on the required depth of shade.

Thus a heavy shade of Indigo may be passed through six vats, starting with a weak and finishing in a strong vat. By this method the best results as regards washing and rubbing fastness are obtained. When lime is used as the alkali the yarn should be soured with hydrochloric acid after dyeing, to remove the lime as calcium chloride. This treatment, or steaming, raises the bronze in Indigo shades which is a feature often demanded. For heavy piece goods the dipping vat is used, whilst light goods may be dyed on the under surface jig or in continuous machines.

VAT DYESTUFFS OTHER THAN INDIGO

At the present time there are a large number of vat dyestuffs available, but of these only a few may be graded as excellent under all the four headings of fastness to light, washing, boiling soda, and chlorine. The gaps in the range are immediately realized when a large range of various fastnesses has to be dyed. A few examples will illustrate this statement. If a lemon-yellow shade is required suitable for casements, it cannot satisfactorily be supplied because all the green toned vat yellows accelerate tendering of the dyed material on exposure to light. Of the safe yellows, Caledon Yellow G (C.I. 1118) is too red and is liable to fade to a black-green shade, whilst Indanthren Yellow 3RT is not a clear yellow and is extremely difficult to dye level in pale shades. Again, if a bright pink or crimson shade is required for casements the deficiencies of the vat range are quickly realized. The Durindone Pinks are not sufficiently fast to light, and, like Indanthren Red FBB, accelerate tendering of the dyed material on exposure to light, whilst Caledon Red BN (C.I. 1162) is too flat for many of the required shades and also produces tendering under some conditions of exposure. It is constantly found that a shade could be obtained by mixing a cold dyeing weak alkali type dyestuff with a hot dyeing strong alkali type dyestuff, but such combinations never dye too satisfactorily owing to their varying rates of dyeing and therefore do not give uniform penetration.

The dyer must, therefore, proceed very warily when choosing vat dyestuffs for specific purposes or he may be quickly in trouble. Again when it is necessary to mix vat dyestuffs for

compound shades still more care must be exercised, as sometimes abnormal results in fastness are obtained. For this reason it is the experience of the authors that it is very necessary to test each mixing for the specific fastness required before proceeding to bulk work.

During the past few years much attention has been given to some apparently abnormal tendering and fading actions brought about by the vat dyestuffs, and this work has demonstrated the interesting fact that the most active in this respect are, in general, the yellows and oranges. The effects produced by these actions are :

1. *Abnormal Fading.*—When mixtures of blue and yellow vat dyestuffs are dyed in combinations it is found that frequently the light fastness of the blue component is reduced by the presence of the yellow. This behaviour is well known with Indanthren Blue GC (C.I. 1115) and Anthraflavone GC (C.I. 1095) (Konig, *J.S.D.C.,* 1913, p. 370 ; Jones, *ibid.,* 1923, p. 202). If these dyestuffs are dyed as self shades and as a mixture and exposed to light it will be found that the blue is much faster than the yellow in a self shade, but that the blue in the mixture fades very badly on a comparatively short exposure.

2. *Tendering During Dyeing.*—In 1928 Scholefield and Patel (*J.S.D.C.,* 1928, p. 268) first drew attention to the fact that tendering of cellulosic material takes place during the dyeing process with vat yellows (excepting Caledon Yellow G type), oranges, and reds if the material is exposed to light and air whilst saturated with the leuco vat solution, or that if a second dyestuff, *e.g.* Ciba Blue 2B is present, this dyestuff is wholly or partially destroyed. After a closer examination of this effect it was concluded that the tendering action of the leuco compound was associated with its reoxidation by air in the presence of light, and the suggestion was made that the auto-oxidation of the reduced dyestuff produced hydrogen peroxide, and that this substance in the presence of light and the oxidized dyestuff caused degradation of the cellulose (see also Landolt, *Textilber,* 1929, p. 533). This was confirmed by saturating fully oxidized active dyestuffs with hydrogen peroxide and exposing when it was found that the cellulose was tendered to an extent depending on the dyestuff present. Similar results were obtained by replacing the

hydrogen peroxide by hypochlorite solutions. For details of the work on this subject the following papers should be consulted : Scholefield and Patel, *J.S.D.C.*, 1929, p. 175 ; Scholefield and Turner, *J. Text. Inst.*, 1933, 24, p. 130 ; Turner, Naber, and Scholefield, *J.S.D.C.*, 1935, p. 5 ; 1937, p. 5.

It has been shown (Whittaker, *J.S.D.C.*, 1935, p. 123) that degradation of viscose rayon during dyeing with vat dyestuffs on the Gerber machine can be very simply prevented by the use of 0·25 per cent. solution sulphite cellulose waste liquor in the dye-bath, whilst the I.G. have patented the addition of tannic acid to the dyebath for this purpose, 0·2–0·4 gms. per litre being sufficient. Both of these additions are very effective in the authors' experience. In these cases the sulphite cellulose liquor or tannic acid is presumably oxidized instead of the rayon.

Tendering during Bleaching.—It has been shown by Derrett-Smith and Nodder (*J. Text.*, 1932, 23, T.293) that when cotton materials dyed with yellow (including the Indanthren Yellow G. type) orange and red vat dyestuffs are exposed to light whilst in contact with hypochlorite bleach liquors the cotton is chemically attacked to a greater extent than when it is undyed or dyed with blue or green vat dyestuffs. On the other hand if the dyeings are treated with the hypochlorite bleach liquor in the dark they show no more tendering than does the undyed material. This effect is greater if the pH of the bleaching liquor is neutral or on the acid side than if it is on the alkaline side, so that to avoid tendering during bleaching of coloured goods it is essential that exposure of the goods to light, particularly sunlight, should be avoided, whilst the sodium hypochlorite liquor used should be kept on the alkaline side by the addition of soda ash, as such an addition does not impair its bleaching efficiency for coloured work.

Tendering during Exposure to Light and Atmosphere.—It has been known for many years that cellulose on exposure to light and atmosphere becomes tender, and this has been attributed to the formation of oxy-cellulose (Witz, *Bull. Soc. Inc. Rouen*, 1883, p. 188 ; Harrison, *J.S.D.C.*, 1912, p. 225 ; 1917, p. 17). During the past few years cases of tendering of vat dyed casement fabrics have been reported, many of which have concerned viscose rayon fabrics. As fabrics containing rayon are usually of lighter construction than all-cotton fabrics, and as viscose rayon is initially

weaker than cotton, when tendering does take place the rayon is liable to give way first although the cotton has been degraded to an equal or greater extent. This position created an unjust prejudice against the use of viscose rayon, instead of the blame being attached to the correct cause, namely, the use of certain vat dyestuffs, chiefly yellows and oranges. With a view to removing this unjust prejudice, work on this problem was undertaken by the Research Departments of Courtaulds, Ltd., and papers on this subject have been published by Whittaker (*J.S.D.C.*, 1933, p. 9; 1935, p. 117; *J.S.C.I.*, 1933, p. T.140). This work has shown that, providing rayon is dyed with dyestuffs that do not accelerate the tendering of cellulose, viscose rayon is eminently suitable for casement fabrics, and that certain dyestuffs actually have an inhibiting effect on the tendering of cellulose. With the co-operation of the dyestuff manufacturers the following agreed list of those vat dyestuffs which, in the light of present knowledge, might be considered safe for the dyeing of shades on casement fabrics without fear of subsequent tendering was published in October, 1932, by the Employers' Federation of Dyers and Finishers, 2, Cooper Street, Manchester, 2.

Caledon Yellow GS, R, 5RS
,,   Gold Orange 3GS
,,   Orange 5RS, 3RS
,,   Brilliant Orange 4RS
,,   Red 2GS, 5GS, 3GNS, BNS, X5BS
,,   Red Violet 2RNS
,,   Brown XRS, RS, HR, ER, HG, 2G, EG, GS
,,   Olive RS, 2BS, 3GS
,,   Brilliant Purple 2RS, 4RS
,,   Brilliant Violet RS, 2BS
,,   Violet XBNS
,,   Dark Blue 2RDS, WFS, 3BS, BMS
,,   Brilliant Blue RS, 3GS
,,   Blue RS, RCS, GCPS, 3GS
,,   Green 2BS, RCS
,,   Jade Green BS, XS
,,   Grey 2RDS, 3GS
,,   Black 2BS, NBS, BS, 2BMS, BGD
,,   Direct Black ACS
Tinon Chlorine Yellow RG
,,   Chlorine Red B2R, BN
,,   Chlorine Red Violet 2RN, RR
,,   Chlorine Dark Blue BO
,,   Dark Blue MB
,,   Blue B2G

Tinon Chlorine Blue RC, GCD, 2G, 3G, 3GF, RS
,,   Chlorine Brown B, BG, B2R, R, V
,,   Grey BN, GN, RN
,,   Chlorine Olive B, G
,,   Olive 2G
,,   Chlorine Green B, G
,,   Black B
,,   Chlorine Black BA, BF, EA, EF, 2B, 2G, 2GR
Cibanone Yellow G, GN, 3R
,,   Golden Orange 3G
,,   Red 4B, RK (BN)
,,   Red Violet 2RN
,,   Violet R, 2R, 2RB, 4R
,,   Brilliant Violet R
,,   Dark Blue BO.MB
,,   Navy Blue RA, GA
,,   Blue B2G, G, GL (RC), GCD, GF, 2G, 3G, 3GF, and RS
,,   Brown B, BG, B2R, G, GG, GR, R, and V
,,   Grey 2B, BN, GN, RA, RN, GA
,,   Olive B, G, 2G, and 2R
,,   Green B and G
,,   Black, B, BA, BF, FA, EF, 2B, 2G, 2GR

Sandothrene Yellow NGN
,,   Red N4B, EBN
,,   Red Violet E2RN
,,   Violet NR, N2R, N4R
,,   Dark Blue NBO, NMB
,,   Blue   ERC,   EGCD, ERS, NRSN, N2G, NGL, N3G, NGCDN
,,   Tetra Blue N2GB
,,   Brown G, NR
,,   Tetra Brown NB, NB2R
,,   Tetra Grey NBN, NGN, NRN
,,   Olive NB, NG
,,   Tetra Olive N2G
,,   Green NG
,,   Tetra Green NB
,,   Black NBA, NEA, N2B, N2G
,,   Tetra Black NB

Paradone Yellow G
,,   Red Violet 2RN
,,   Brilliant Violet 2R
,,   Violet BR, B
,,   Blue GCD, RC, FC, RS
,,   Dark Blue
,,   Black 2B
,,   Direct Black R, BG
,,   Grey B, R

Indanthren Yellow G, 3R, 3RT

Indanthren Brilliant Orange GK, GR, RK
,,   Golden Orange 3G
,,   Orange F3R, 7RK
,,   Scarlet GG
,,   Red GG, RK, BK, FBB
,,   Pink FBBL, B
,,   Red Violet RRK
,,   Corinth RK
,,   Brilliant Violet RK, BBK
,,   Violet FFBN
,,   Dark Blue BOA, BO
,,   Navy Blue BRF, R, G
,,   Blue RK, RSN, G, D, BC, 3G, 3GT, 5G, 8GK
,,   Brilliant Blue R, RCL, 3G
,,   Blue Green FFB
,,   Green BB, GT, G
,,   Brilliant Green B, FFB, GG, 4G
,,   Olive Green B
,,   Olive, R, 3G
,,   Khaki GG
,,   Yellow Brown 3G
,,   Brown R, FFR, 3R, BR, G, GG, 3GT
,,   Red Brown 5RF
,,   Grey K, BTR, RRH, 3B, 6B, BG, M
,,   Direct Black RB
,,   Black BB, BGA

In this connection a paper by Jones (*J.S.D.C.*, 1936, p. 285) should be read in which evidence is put forward that cellulose even when dyed with safe dyestuffs may be tendered due to atmospheric pollution, the sulphur dioxide and nitrogen peroxide present in a polluted atmosphere in the presence of moisture producing sulphuric acid by a "lead chamber" reaction. In such cases the dyer's responsibility cannot reasonably be extended to more than the use of dyestuffs which do not accelerate the tendering of cellulose and their application to the fibre in the proper manner.

These abnormal fading and tendering actions brought about by the vat dyestuffs must be fundamentally connected with each other, but at the present time no satisfactory theory has been put forward which can be said to correlate all the available facts.

Attention was called at the beginning of this section to the fact that all vat dyestuffs are not fast, but many are extremely fast to light, washing or boiling soap. Some are also fast to chlorine, so that they may be used in colour-woven goods which have subsequently to be bleached. Special methods have to be adopted

for boiling out the goods, since very few will stand boiling in a pressure kier without marking off. In fact, it was frequently found in an open kier that the pieces at the bottom which had had the weight of the other pieces on them had marked off, whilst those at the top had come out perfect. This is due to the fact that the alkali plus the impurities removed from the cloth form a local vat with the dyestuff and cause it to mark off.

These dyestuffs are, however, otherwise so valuable that the trade has adapted its technique to the fact that it is necessary to take special precautions in the boiling-out process. The severity of the process is determined by preliminary tests. In some cases a boiling in the open jigger is all the boiling that is given. Other bleachers do not boil the goods, but plait them down into a soap and soda liquor at 90° C. and allow them to steep, a treatment which reduces the liability to mark-off to a minimum. Again, some dyestuffs whilst not bleeding off, undergo a change of shade in the bleaching liquor, but in such cases the original shade may usually be restored by a simple after-treatment with hydrosulphite at room temperature, unless excessive over-bleaching has occurred. Many products have been suggested as additions to the kier to prevent marking off, Resist Salt L being one of the best known.

APPLICATION

The successful application of the vat dyestuffs has been a source of great trouble to the dyer, but the experience now accumulated has reduced the difficulties encountered. One of the most important factors in the dyeing of vat dyestuffs is intelligent manipulation. In no other branch of dyeing is it so necessary to avoid any slackness : the operatives require to be specially trained for the job, since slovenly work inevitably means faulty results. It is essential to avoid the use of hard water as far as local circumstances will permit ; in this connection the use of Calgon T will be found to be advantageous. If hard water is used in setting the vat a scum will be formed, and this must be completely removed before the material is entered. A small but important point is to see that the water-pipe reaches to the bottom of the dyebath so that as the bath is filled with

water air is not taken in, as always happens if the water is allowed to splash into the dyebath from above. This precaution reduces the amount of scum produced. The use of copper and brass must be avoided because they decompose the sodium hydrosulphite with the formation of black copper sulphide which is liable to stain the goods being dyed. Once dyeing has started it must be carried right through and not allowed to hang about at any intermediate stage, particularly if a shade is being repeated, whilst the time and temperature of vatting, and the time and method of oxidation must be kept the same. In dyeing compound shades, dyestuffs of the same rate of dyeing should be chosen as far as possible, and dyestuffs which require various strengths of alkali should never be mixed if it is possible to avoid doing so, because the results are never good. Trouble may also be caused by the fact that one dyestuff dyes better at a different temperature to the other; in such cases dyers usually dye at an intermediate temperature. When dyeing compound shades it is best to reduce each dyestuff separately and mix them in the dyebath in the reduced state rather than to mix them in the unreduced state and then reduce them. By this means one is better able to judge if each dyestuff is properly reduced.

From the point of view of application the vat dyestuffs may be divided into :

1. Dyestuffs which require a strongly alkaline vat, viz. $1-1\frac{1}{4}$ gallons caustic soda, 76° Tw. per 100 gallons dye liquor.

2. Dyestuffs which require a weakly alkaline vat, viz. $2\frac{1}{2}-4$ pints caustic soda, 76° Tw., per 100 gallons dye liquor.

3. Dyestuffs of the Indigoid class which have varying conditions for the various members, but which may be summed up as weak alkali, but requiring more hydrosulphite than 2. This class is also always made up in stock vat form, whereas 1 and 2 may be reduced in the actual dye bath.

Certain vat dyestuffs require different amounts of caustic soda to those given, e.g. Indanthren Brilliant Orange GR requires the use of 2 gallons caustic soda 76° Tw. per 100 gallons of dyeliquor. In general 3–6 lb. sodium hydrosulphite per 100 gallons of dyeliquor is used, the actual amount depending on the depth of shade to be dyed.

The older vat dyestuff powders required to be thoroughly wetted out by pasting with Turkey Red Oil, one of the proprietary wetting agents, or methylated spirit, but most of the present-day powders are readily wetted with hot water alone ; a point to which the dyestuff manufacturers have applied successful research.

The actual dyebath may be made up in various ways according to the material being dyed. The caustic soda and hydrosulphite may be added to the dyebath at 60° C., the dyestuff added in paste form through a fine sieve, and the dyeliquor gently stirred and allowed to stand (usually for 20 minutes) till the dyestuff is reduced.

An alternative method is to prepare a stock vat as follows : 8 oz. of dyestuff powder are pasted with hot water and made up to 2 gallons with water at 60°–65° C., ¾ pint NaOH 70° Tw. added and 2 oz. sodium hydrosulphite powder stirred in gradually. Vatting is allowed to take place for 10–15 minutes at 60° C. in this stock vat before adding to the dyebath at the dyeing temperature, which has been prepared with the remaining caustic soda and one-half of the sodium hydrosulphite ; vatting is continued in the dyebath for 20 minutes. The remaining hydrosulphite is added just before dyeing commences. Thorough stirring is essential at all stages. Individual dyestuffs may require some variation in details from this process, *e.g.* Indanthren Brilliant Orange GR is vatted at 80° C. Again when stock vatting the Durindone Pinks the suspension containing the caustic soda is actually boiled and the hydrosulphite added immediately the steam is turned off.

Some dyestuffs require to be allowed to vat for a much longer time than others in order to get the best value out of the dyestuff : Caledon Green B and Indanthren Yellow 3RT are two examples which are better for prolonged vatting. When, as is the case with Caledon Yellow G, the leuco compound is a distinctive shade, viz. blue, it is easy to see if the bath is reduced, but with some dyestuffs like Caledon Blue RC, whose leuco compound is blue, it is difficult to tell if the dyestuff is satisfactorily reduced till one becomes experienced. Three methods may be adopted. Spotting on a white porcelain tile is one method ; dipping a piece of ground glass in the vat, then lifting out and noticing the colour of the liquor as it drops off, is a second one. The third one is used by the authors and consists of drawing out some of the vat in a test

tube, and looking through it at the light with a magnifying glass. The solution should not only be the colour of the leuco compound, but should be perfectly clear : if particles are visible the vat is not in correct condition.

Of the three classes of dyestuffs referred to above, the dyeing of cotton with No. 1 class is usually started at 35° C. and the temperature raised to 50°–60° C. No. 2 class includes some dyestuffs which are best applied at the same temperature as the No. 1 class and some which require to be dyed cold, but as their affinity for cotton is so much less than the No. 1 class dyestuffs large additions of common salt are usually required in order to get heavy shades. The class 3 dyestuffs are applied, in general, by the method used for class 2 dyestuffs ; they are the easiest class to dye, but unfortunately their fastness does not fulfil the highest requirements.

Dyeings of the vat dyestuffs may be oxidized in the air after squeezing or wringing, but oxidation may be accelerated by after-treatment with bichrome and sulphuric acid, sodium hypochlorite, or sodium perborate, of which sodium hypochlorite is the most rapid. These after-treatments are particularly advisable in the case of Caledon Yellow G which oxidizes in the air rather slowly. If perborate is used as an oxidizing agent it should be remembered that though the shades obtained are usually brighter than those which are air oxidized they are frequently less fast. In the case of Indanthren Blue 5G, Caledon Brilliant Violet 2BS, and Caledon Khaki GG souring after oxidizing and prior to soaping is essential to produce the correct shade. In no case must the material be soured before the oxidation of the leuco compound is complete, or a poor result will be obtained. After oxidation the dyeings require to be washed off, soured, given a rinse in cold water, then in hot water, and finally well soaped for $\frac{1}{2}$ hour at the boil using 2–3 lb. soap and 1 lb. soda ash per 100 gallons.

Soaping in most cases aggregates the dyestuff on the fibre (Bean and Rowe, *J.S.D.C.*, 1939, p. 67 ; Valkó, *J. Amer. Chem. Soc.*, 1941, p. 1436) and is essential for the complete development of shade and fastness. Should any difficulty be experienced in removing loose dyestuff from the interstices of multiple twist yarns the method of steep soaping described on p. 181 should be used. With certain dyestuff, *e.g.* Indanthren Olive Green B and

certain Indanthren Blues, over-oxidation of the dyestuff may occur, so that the true shade is not obtained even on soaping. This difficulty may be overcome by treatment with 2–3 lb. soap, 2 lb. soda ash, and 5 lb. glucose per 100 gallons water.

Faulty vat dyeings are always difficult to correct and require considerable judgment on the part of the foreman dyer as to the best method to be adopted. Unlevel dyeings may be treated for 20 minutes at 60° C. in a " blank " vat containing the amounts of caustic soda and sodium hydrosulphite used in the original dyeing. With some dyestuffs there is no appreciable loss in depth of shade by this treatment, but more usually some stripping of dyestuff occurs and the material then requires to be shaded to pattern. If the material is too heavily dyed and cannot be stripped sufficiently by the above treatment the addition of one of the vat restraining agents (see Section XVII.) will be found to be of assistance.

Cotton.—Formerly loose cotton was commonly dyed in the usual open vat provided with a detachable wire basket which may be mechanically tilted so that the material may be conveniently placed on the travelling feeder of the squeezing rollers through which the cotton is passed from the dyebath. The cotton is then allowed to smother until oxidation is complete. At the present time cotton in the loose form and also as sliver is usually dyed in pack machines, *e.g.* in the Obermaier machine, into which it is packed uniformly and firmly. If the dyeing machine is fitted with a hydro-extracting arrangement the cotton is boiled out in the machine, hydro-extracted, and then dyed. The dyeing is then finished by hydro-extracting, oxidizing either by forcing compressed air through the material or with a suitable oxidizing agent, and washing off. Finally the cotton should be softened so that it will not cause trouble on the cards.

Cops, cheeses, roving bobbins, and warp beams are frequently dyed in one of the many forms of dyeing machines, usually of the spindle type, a water sealed pump not drawing air, and efficient circulation being essential for satisfactory dyeings.

Yarn may be satisfactorily dyed on sticks, on machines of the roller type, or in pack machines like loose cotton. When dyeing on sticks straight sticks may be used providing the sticks are not held too far above the surface of the dyeliquor. Bent sticks,

although theoretically advantageous, are more difficult to use unless very carefully manipulated, as the yarn is liable to float and become entangled. After dyeing the yarn may be squeezed through a pair of sticks, wrung out on a peg, or passed through squeezing rollers, and then hung out to air oxidize. Whilst oxidizing the yarn should be turned occasionally in order to prevent liquor from draining to one end of the yarn and so causing trouble. Most shades on cotton can be dyed on the roller type of machine providing an increased quantity of sodium hydrosulphite is used in preparing the dyebath. By the use of these machines the whole of a batch of yarn can be entered into the dyeliquor at the same time, which is impossible when dyeing on sticks, whilst labour costs are considerably reduced since the yarn is turned mechanically instead of by hand. After dyeing the yarn is not wrung out but is oxidized on the machine by oxidizing agents, sodium hypochlorite, when its use is permissible, being very effective. The yarn is then rinsed in cold water, soured, rinsed in hot water, and finally soaped.

Warps are usually dyed on a two-box machine in four ends, then oxidized, soured, and soaped in a long box machine in one run. They may also be dyed in one of the many forms of pack machines.

Cotton pieces may be dyed by three methods, viz. :

    1. On the jigger.

    2. On the pad.

    3. Combination of pad and jigger.

    1. This method is one of the most common dyeing methods, particularly for dark shades, and is the most reliable for matching to shade. It is applicable to most types of cloth, the exceptions being light-weight cloths which have a tendency to stretch; certain of these cloths may be dyed on tensionless jigs. The following method is one used in practice for dyeing pieces with vat dyestuffs. By this method the dyestuff is added in two portions, though it may be added in four ends if it is thought advisable. The dyestuff is stirred into a paste with two-thirds of the caustic soda and half the sodium hydrosulphite plus a little water at 60° C. To the jig are then added the remaining one-third of the caustic soda and half of the remainder of the hydrosulphite, half of the vatted dyestuff added, and the piece given one end, the

remaining hydrosulphite and vatted dyestuff added, and the piece given another end. Dyeing is then completed in five ends, the temperature of the dyebath being maintained at 60° C. After dyeing the piece is given three ends in a chrome bath containing 2·5 per cent. bichrome which is added in two lots, three ends in running water, three ends in sours, four ends in boiling soap and soda, and finally three ends in running water. The experience of the dyer, however, plays a great part in the methods employed, and many variations of the above method are to be found. Some dyers use jigs fitted with nip rollers, some dispense with nip rollers ; some run the pieces straight into the chrome bath without any preliminary wash, others do not use chrome ; some prepare the pieces in soap or soluble oil, others do not ; yet they all get results which satisfy the trade requirements.

When preparing pieces for dyeing on the jigger, care must be taken to see they are run straight on the batching rollers or bad selvedges will result due to oxidation, a tendency which is very much reduced by the addition of sulphite waste liquor or tannic acid, which retard the rate of oxidation. All scum must be removed from the surface of the dyeliquor and the pieces run so that there is no splashing, which would be liable to produce spots on the pieces. The roll of cloth on the beams should not be stationary for any length of time, or the dyestuff solution will drain to the bottom of the roll and cause bar effects on the finished goods. When a stop has to be made the tapes should be untied from the end-cloth and the roll allowed to revolve or swing until it is ready to be again run in the liquor. The size of the plug hole of the jig and the water supply pipe must be such as to permit rapid emptying and filling up of the dyebath. Speed of manipulation is essential.

2. The padding machine may be used for light shades on light-weight cloths. The two-bowl type with rubber-covered bowls may be used, but the three-bowl type which gives a double nip is preferable. It is essential to see that the surface of the bowls is perfect or streakiness will result. After leaving the squeezing rollers on the machine the goods are given an air passage, or plaited down and left lying for about ½ hour. They are then oxidized, rinsed, and soaped at the boil.

3. The principle of this method is to pad the dry cloth with a

very fine dispersion of the vat dyestuffs, well squeeze or dry the cloth, and then reduce the dyestuff in a jigger with the necessary quantity of caustic soda and hydrosulphite. The dyestuffs used must be very finely ground in order to get an even impregnation of the cloth, and specially fine powders (Type 8059) have been prepared for this purpose. Prestabit Oil V or Calsolene Oil HS, which are highly sulphonated castor oils, is used to paste up the dyestuff, and has the property of carrying the suspended dyestuff into the inside of the fibre. The colour box should be provided with a steam coil and a guide roller, whilst propellers at both ends of the guide roller are recommended to prevent settling-out of the padding liquor during the padding process. The end-cloth should not be too short, and thick seams should be avoided. Absorption of dyestuff during padding depends not only upon the squeezing effect of the nip-rollers but on the quality and moisture content of the goods, the running speed and temperature of the padding liquor. One or more runs through the padding liquor at $70°-80°$ C. are usually given, followed by eight to ten ends on the jigger in a reducing liquor of caustic soda and hydrosulphite at $50°-60°$ C., after which the goods are oxidized, rinsed, soaped, and finally rinsed. (See also Hopkins, *J.S.D.C.*, 1941, p. 358.)

Linen.—Since linen in the grey state contains 25–30 per cent. of impurities it is seldom dyed with vat dyestuffs in this state, but is usually given a previous bleaching treatment. This applies to the dyeing of linen both in yarn and piece form. These dyestuffs are applied to linen yarns by the same methods used for cotton excepting that as the vat dyestuffs exhaust more rapidly on linen than on cotton larger quantities of restraining agents, when these are used, are required. Light weight fabrics may be dyed by ordinary methods on jiggers but with heavier materials penetration is only obtained by the pigment padding process using ordinary 2 and 3 bowl mangles with rubber rollers. For further details on the dyeing of linen with vat dyestuffs see Montgomery (*J.S.D.C.*, 1938, p. 351).

Viscose Rayon.—The vat dyestuffs present many difficulties to the rayon dyer owing to the great affinity of the fibre for them and no experienced dyer would deny that his results still leave much room for improvement. The greatest skill is required in manipulation in order to get passable results because it has to

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be admitted that the average vat shade on viscose rayon is of a lower standard of levelness than when dyed with all other classes of dyestuffs excepting the sulphur dyestuffs.

Like all other classes of dyestuffs the individual members of the vat dyestuffs vary considerably in their behaviour to viscose rayon, and this has necessitated a detailed examination of their dyeing properties. Whittaker (*J.S.C.I.*, 1932, p. 66T) has published an empirical method which enables the vat dyestuffs to be grouped into three classes. This method is based on the relative behaviour of 150/21 and 150/36 viscose yarns when dyed in the same dyebath. As the reliability of this test depends upon a constant difference in the dyeing and optical behaviour of the yarns which may vary with different lots of yarn it has now been superseded by the " 1 minute strike test " (Whittaker, *J.S.D.C.*, 1938, p. 258). This test, which has not the limitations of the above test and which is within the scope of the most poorly equipped dyehouse laboratory, has more recently been critically examined and correlated with diffusion and exhaustion rate data by Boulton and Morton (*J.S.D.C.*, 1939, p. 481). In carrying out this test a series of 40 volume dyebaths (200 c.c.) is prepared each to accommodate two small skeins of yarn or slips of fabric (2·5 gms. each). It is only possible to obtain a series of dyebaths of the necessary uniformity by preparing a bulk vat dyebath and then measuring out the required number of 200 c.c. portions, whilst the viscose skeins must be wound from the same large commercial skein. The dyeliquors are then brought to 60° C., one skein entered into the dyeliquor exactly 1 minute before the other and dyeing continued for 5, 20, 40, 60, and 80 minutes. After similarly oxidizing, soaping, and drying, the two skeins from each dyebath are then knitted in alternate broad panels on a single thread circular stocking knitting machine and examined. From the 5 minute dyeings the strike difference is judged and designated by a letter, viz. :

(A) There is no appreciable difference in depth of shade between the two skeins.
(B) There is appreciable difference.
(C) There is very marked difference.
(D) There is gross difference, as between full dyeing and light staining.

The remaining dyeings are taken, examined and to the letter indicating the original strike difference is now appended the time required for the two skeins to attain the same depth. Examples of complete strike indexes are :

A5 = level after 5 minutes.

A/B.40 = very slight strike difference ; level after 40 minutes.

C40 = Marked strike difference ; level after 40 minutes.

C∞ = Marked strike difference ; not level after 80 minutes.

D∞ = Gross strike difference ; not level after 80 minutes.

A finer classification of the rapidly exhausting " strong alkali " dyestuffs is obtained with the " modified " or " 10 second strike test." This only differs from the " 1 minute strike test " in that one skein is entered into the dyebath 10 seconds before the second skein instead of after 1 minute. The results of the strike tests are given in the following tables :

STRIKE INDEX CLASSIFICATION

No.	" Weak alkali " dyes	Strike test
1	Indanthren Yellow GK	A5
2	Indanthren Yellow 4GK	A5
3	Caledon Yellow 3G	A/B40
4	Indanthren Orange 2RK	B20
5	Indanthren Red BK	B20
6	Indanthren Olive 3G	B20
7	Caledon Red 5G	B20
8	Indanthren Yellow FFRK	B20
9	Caledon Red Violet 2RN	B20
10	Paradone Yellow 5GK	B20
11	Indanthren Yellow 7GK	B20
12	Indanthren Corinth RK	B40
13	Indanthren Orange 3G	B40
14	Indanthren Yellow Brown 3G	B80
15	Caledon Red X5BS	C20
16	Hydron Orange RF	C20
17	Hydron Violet 2BF	C20
18	Caledon Brilliant Violet R	C20
19	Caledon Red 5B	C20
20	Caledon Brilliant Violet 2BS	C20
21	Indanthren Pink B	C40
22	Indanthren Yellow RK	. C80
23	Indanthren Brown FFR	C80
24	Caledon Brown G .	C80
25	Hydron Blue R	C80
26	Caledon Dark Brown 4RBS	C80
27	Caledon Brown RS	C∞
28	Indanthren Olive GN	C∞
29	Caledon Olive RS	C∞
30	Indanthren Brown BR	C∞
31	Indanthren Red Brown 5RF	C∞
32	Indanthren Bordeaux B	C∞
33	Indanthren Red FBB	C∞
34	Caledon Red BN	D40

STRIKE INDEX CLASSIFICATION

No.	*"Weak alkali" dyes*	*Strike test*
35	Ciba Violet B	D_{40}
36	Indanthren Brilliant Orange RK	D_{40}
37	Indanthren Orange F3R	D_{80}
38	Caledon Red 2G	D_{80}
39	Indanthren Printing Violet RF	D_{80}
40	Caledon Gold Orange G	D_{80}
41	Hydron Scarlet 2B	D_{80}
42	Indanthren Brown RRD	D_{80}
43	Indanthren Orange 2R	D_{∞}
44	Hydron Bordeaux B.	D_{∞}
45	Indanthren Rubine B	D_{∞}
46	Indanthren Magenta B	D_{∞}
47	Ciba Brown 2R	D_{∞}
48	Ciba Blue 2B	D_{∞}
49	Hydron Blue G	D_{∞}
50	Durindon Pink FFS	D_{∞}
51	Durindon Pink FB	D_{∞}

No.	*"Strong alkali" dyes*	*Strike test (1 min.)*	*Modified strike test (10 sec.)*
1	Indanthren Khaki 2G	A_5	5
2	Cibanone Yellow 2GR	B_{20}	5
3	Hydron Yellow NF	B_{20}	10
4	Cibanone Red 4B	B_{40}	5
5	Cibanone Blue 2G	B_{40}	5/10
6	Indanthren Yellow 3RT	B_{40}	10
7	Paradone Yellow GC	B_{∞}	20
8	Paradone Yellow G	C_{40}	60
9	Indanthren Scarlet GK	C_{80}	5
10	Indanthren Brown GR	D_{80}	20
11	Paradone Violet 2R	D_{∞}	20
12	Indanthren Grey M	D_{∞}	20
13	Caledon Green RC	D_{∞}	60
14	Indanthren Direct Black RB	D_{∞}	60
15	Indanthren Blue 5G	D_{∞}	60
16	Caledon Orange 4R	D_{∞}	60
17	Indanthren Olive Green 2G	D_{∞}	60
18	Alizanthrene Navy Blue	D_{∞}	80
19	Caledon Orange RRT	D_{∞}	80
20	Caledon Jade Green X	D_{∞}	80
21	Cibanone Black 2B	D_{∞}	∞
22	Paradone Dark Blue	D_{∞}	∞
23	Indanthren Brilliant Violet 3B	D_{∞}	∞
24	Caledon Blue RC	D_{∞}	∞
25	Indanthren Olive Green B	D_{∞}	—
26	Paradone Black 2B	D_{∞}	∞
27	Caledon Blue RS	D_{∞}	—
28	Indanthren Grey 3B	D_{∞}	—
29	Indanthren Grey MG	D_{∞}	∞
30	Indanthren Scarlet 2G	D_{∞}	∞

In order to obtain the most satisfactory dyeings with mixtures, dyestuffs having the same properties, rate of dyeing or affinity and levelling speed, should be used, *i.e.* those having the same

strike index. As the choice of vat dyestuffs is limited this is not always possible ; in such cases it should be appreciated that the levelling speed is of more importance than the exhaustion rate. Experience has also shown that it is inadvisable to mix " strong alkali " and " weak alkali " dyestuffs in compound shades owing to their differing dyeing properties. In general, it may be stated that the " strong alkali " dyestuffs exhaust more rapidly and have poorer levelling properties than the " weak alkali " dyestuffs. For this reason it is advisable to add a restraining agent when dyeing viscose rayon with " strong alkali " dyestuffs, whereas such an addition is unnecessary when dyeing the " weak alkali " vat dyestuffs. Protectol II liquid, Peregal O, Albatex PO, glue, certain sulphite cellulose waste liquors, and polyvinyl alcohol are all used for this purpose (see Section XVII.) : the strike test enables the true comparative value of these auxiliary products as vat restraining agents to be evaluated. It must be remembered that the use of sulphite cellulose waste liquor, for instance, requires the use of more vat dyestuff to obtain the same depth of shade than in its absence, because it prevents complete exhaustion of the dyebath.

Two methods are recommended by the dyestuff makers for the application of the " weak alkali " vat dyestuffs on cotton ; thus the I.G. designate as IK dyestuffs those dyestuffs which are recommended for dyeing cold. When dyeing viscose yarns, however, practical experience has shown that the cold dyeing (IK) method is unsatisfactory, as by dyeing cold any light and dark dyeing variations are emphasized, and very little levelling is obtained until higher temperatures are reached. Experience has also shown that a satisfactory method for both the IK and IW vat dyestuffs is to commence dyeing at 35° C., and then raise the temperature of the dyebath to 60° C. With some IW dyestuffs, Indanthren Gold Orange 3G, better results are obtained by dyeing throughout at 80° C. using twice the recommended amount of caustic soda, tannic acid being used to prevent tendering of the viscose during the dyeing operation.

Viscose yarns may be dyed in the ordinary dye-beck or on machines of the roller type, such as the Gerber machine, whilst piece-goods may be dyed on the padding machine or on the jigger. It is clear from the practical application of vat dyestuffs that the

dyeing of piece-goods is simpler than the dyeing of skeins for mechanical reasons. Pieces when padded or jig dyed enter the dye-liquor as a flat surface, whereas skeins enter as a bunch of threads, so that even penetration is much more difficult to obtain. For this reason when dyeing viscose skeins on the Gerber machine improved results are obtained by hand turning the skeins as the rollers rotate so as to open out the skeins. Such hand turning requires to be carefully carried out by experienced workmen to avoid any damage to the yarn.

It is the authors' experience that on viscose rayon yarns the weak alkali vat dyestuffs are the most difficult to finish satis-factorily as owing to the ready solubility in the leuco form they are liable to run or to be washed off the fibre during the oxidation and soaping processes. One of the fundamental manipulation difficulties is due to the obvious fact that rayon skeins cannot be wrung out of the alkaline vat in similar manner to cotton yarns before air-oxidation by hanging ; moreover, it is impossible to hydro-extract rayon skeins uniformly. Rayon threads when wet also remain bunched together much more persistently than cotton so that more time is required to air oxidize vat dyestuffs on rayon by hanging than on cotton, whilst the shaking out of wet rayon skeins is inadvisable as this is liable to result in strained yarn. Traces of hydrosulphite (this reputed unstable body will be found to very stable in very dilute solution) may, therefore, be left on the yarn, and when it is washed and soaped it frequently happens that there are sufficient traces of hydrosulphite remaining locally to dissolve off some dyestuff and so produce a patchy or streaky dyeing. In order to overcome these difficulties oxidizing agents may be used. Practical experience has shown that in most cases the best method is to oxidize with dilute sodium hypo-chlorite (0·25 c.c. NaOCl (15 per cent. available chlorine) per 100 c.c. liquor) in presence of sufficient common salt to give a 2 per cent. solution, give a cold wash, sour with dilute hydro-chloric acid, followed by a second cold wash, then a hot wash, and finally soap at the boil. The strong alkali vat dyestuffs show much less tendency to wash off during the finishing operations because their leuco compounds oxidize more readily than the leuco compounds of the weak alkali vat dyestuffs, and are therefore easier to manipulate when finishing off.

Cellulose Acetate Rayon.—In order to produce shades on cellulose acetate rayon fast to boiling and degumming vat dye-stuffs have been applied to saponified cellulose acetate rayons (Section XIII.). When these dyestuffs are applied from caustic alkali solutions an added loss in weight and tenacity occurs over that resulting from the saponification treatment. These losses may be reduced to a minimum by the use of milder alkalies, such as trisodium phosphate, sodium carbonate, etc. ; but the method is limited to those dyestuffs which are capable of being vatted with such mild alkalies.

It will be apparent from the above that the dyeing of vat dyestuffs on saponified cellulose acetate rayon is not very satis-factory, and it is not surprising that many other methods not involving prior saponification have been proposed. The dyeing of unsaponified cellulose acetate rayon is essential when if, in addition to fastness to boiling and degumming, dyeings are required fast to viscose cross-dyeing. One method which has given satisfactory results with a wide range of vat dyestuffs has been described by Courtaulds Limited, Whittaker and Wilcock (E.P. 517,751). This method consists of vatting with the recom-mended amounts of caustic soda and sodium hydrosulphite and then adding sufficient sodium bicarbonate to convert all the free caustic soda into sodium carbonate. Vatting is easier and more rapid with caustic soda than with sodium carbonate, and in many cases deeper shades are possible than when vatting is originally effected with sodium carbonate. The addition of a protective colloid, *e.g.* glue, has a beneficial effect in obtaining a satisfactory vat.

Wool.—Wool cannot be dyed without deterioration with the Anthraquinone vat dyestuffs owing to the strongly alkaline nature of the dyebath, though the use of protective colloids such as glue, Protectol, etc., has minimized this deterioration to some extent. The Indigoid vat dyestuffs have been recommended for the dyeing of wool, but so far as Great Britain is concerned the authors have not heard of their wide adoption. This is not sur-prising as there is a large range of wool dyestuffs which meet the normal fastness requirements of the various branches of wool-dyeing satisfactorily which are much cheaper and easier to apply than are the vat dyestuffs. According to Isles (*J.S.D.C.*, Jubilee

issue, 1934, p. 136) the use of vat dyestuffs for high-class suitings is almost negligible, but they are specially suited for striping effects in fine wool delaine shirtings as their fastness to laundering and bleaching is outstanding.

The following recipe is abstracted from the maker's literature and is given as typical recipe :

Stock Vat.—1 lb. Ciba Red 3B powder is made into a paste with 2 oz. Turkey Red Oil and warm water. The paste is then thinned with 10 gallons water at 80° C., $1\frac{1}{2}$ pints caustic soda (66° Tw.) added, $1\frac{1}{2}$ lb. sodium hydrosulphite powder slowly added and allowed to stand for 15 minutes with occasional stirring.

The dyebath is set at 50°–60° C. with $\frac{1}{2}$ lb. freshly dissolved glue, 1 pint 25 per cent. ammonia and 4 oz. sodium hydrosulphite conc. powder per 100 gallons water. The dyestuff in solution is then added through a filter cloth, the bath stirred and dyeing carried out at 50°–60° C. for $\frac{1}{2}$ to $\frac{3}{4}$ hour. In most cases good exhaustion is obtained, but to obtain more complete exhaustion in heavy shades the addition of 2–8 oz. ammonium chloride or sulphate per 100 gallons dyebath may be made. On completion of the dyeing the goods are squeezed off and allowed to oxidize ; the oxidation proceeds rather slowly and up to 2 hours may be necessary. The goods are then washed and soured in a weak boiling acetic acid or formic acid bath or they may be lightly steamed in order to destroy any free sodium hydrosulphite. The development with acid is absolutely necessary for the production of the fastest results. This may be shown by making light exposures of Helindone Pink AN on flannel, one piece being boiled in sulphuric acid to destroy the hydrosulphite and one piece simply washed off. The difference in fastness to light is most marked.

Silk.—The dyeing of vat dyestuffs on silk appears to be carried out to only a very limited extent, mainly on silk yarns for use as effect threads in dress goods, shirtings, and other similar goods. Very little information on this subject has appeared in the literature apart from that supplied by the dyestuff manufacturers. Keyworth (*J.S.D.C.*, 1933, p. 246) however, states that "The affinity of most vat dyes for silk is low, so that the production of dark shades is very expensive. The alkalinity and temperature must be kept low in order to preserve the

strength and lustre of the silk. Addition of a protective agent, *e.g.* Protectol I, is accompanied by a further reduction in the tinctorial power. Again the dyes should be selected to give the most equal exhaustion. According to the makers' instructions, dyeing of degummed silk is begun at the prescribed temperature and is finished in about 1 hour; in actual practice often a much longer time is required. Most vat dyes exhaust slowly on silk, but a few, particularly some pinks and violets exhaust rapidly, and are apt to give unlevel results. Tin weighted silks usually are not dyed with vats, but vat dyed silks can be weighted subsequently."

SOLUBILIZED VAT DYESTUFFS

The solubilized vat dyestuffs are a series of dyestuffs, marketed as the Indigosol and Soledon dyestuffs, which are readily soluble in water, and which may be applied to vegetable and animal fibres without vatting. They are sulphuric esters of leuco vat dyestuffs, and as they belong to the class of phenolic sulphuric esters they are fairly easily decomposed by acids but are stable to alkalies. The first Indigosols (marketed by Durand and Huguenin) were prepared in 1922 by Bader and Sunder from the dry leuco compounds of Indigo and other vat dyestuffs by the use of chlorosulphonic acid in presence of a tertiary base. A great advance was made in 1924 by Scottish Dyes, Ltd., who found that these compounds may be formed from the dyestuff itself by the action of an alkyl ester of chlorosulphonic acid in · presence of a metal and a tertiary base.

Chemically, these dyestuffs may be divided into two groups, those whose parent dyestuffs are Indigoid, and those whose parent dyestuffs are Anthraquinone vat dyestuffs. In this connection it should be noted that the I.G. have adopted the following key letters to the generic name Indigosol :

O for derivatives of Indigo
A ,, ,, ,, Algol dyestuffs
H ,, ,, ,, Helindon dyestuffs
I ,, ,, ,, Indanthren dyestuffs
T ,, ,, ,, Thio-indigo dyestuffs

Solutions of the Indigoid derivatives are either not coloured at all or only slightly, whereas those derived from Anthraquinone vat dyestuffs give comparatively strongly coloured solutions. For the actual colour of the solution of the Indigosols produced up to

October, 1937, see Christ (*J.S.D.C.*, 1938, p. 94). The solubilizing process is said to be capable of application to all vat dyestuffs, but the stability varies widely and some products decompose so rapidly that they may not be stored without decomposition long enough for normal commercial requirements. At the present time, however, the number of available solubilized vat dyestuffs is rather limited, but the range is gradually increasing, mainly by the addition of members whose parent dyestuffs are Anthraquinone vat dyestuffs.

Up to the present time the chief field for the solubilized vat dyestuffs has been in piece dyeing, but as the range is extended their use in other branches of dyeing will no doubt be increased. They are naturally more expensive than the parent vat dyestuff, but Christ (*ibid.*, p. 97) states that in cases of pale dyeings where the cost of the actual dyestuff is very small in comparison with that of the additional chemicals requisite for vat dyestuffs, the Indigosol pad dyeing process is cheaper than the vat pigment padding process. For darker dyeings, however, the proportion changes in favour of the vat dyeings. It is the present authors' practice to make an ever-increasing use of the Soledons and Indigosols in dyeing both viscose and cotton in the skein form on the roller type of skein dyeing machine. All shades are produced with them for which the dyeing price permits as they have many virtues which compensate for their higher price. Experience shows that the time of dyeing is shorter, the shades are more even, there is no danger of oxidation streaks, and the use of caustic soda is avoided. In the cases of many shades the use of common salt makes it possible to reduce the total dyeing cost to the level of that of vat dyestuffs, whilst with certain pale shades the costs are actually less than for vat dyeings.

The affinity of the Soledon and Indigosol dyestuffs for vegetable fibres is in general poor, but, as with all other classes of dyestuffs, they vary widely in their rate of exhaustion, salt sensitivity, and temperature of maximum affinity, as is shown by the following tables :

COMPARISON OF SALT SENSITIVITY AND DEGREE OF EXHAUSTION OF SOLEDON JADE GREEN XS PASTE AND INDIGOSOL BROWN IBR POWDER, WHEN DYED FOR 20 MINUTES AT 50° C. ON " FIBRO," LIQUOR-MATERIAL RATIO 40 : 1

3 per cent. Soledon Jade Green XS paste

Common salt (per cent.)	Nil	2	4	6	10	15
Exhaustion (per cent.)	..	23	45	55	62	70	81

3¾ per cent. Indigosol Brown IBR powder

Common salt (per cent.)	.. Nil	10	20	50	100	200
Exhaustion (per cent.)	.. 4½	24	35	44	53	60

DYEING PROPERTIES OF INDIGOSOL AND SOLEDON DYESTUFFS
Viscose Rayon-liquor ratio=1 : 40

	Rate of dyeing	Tempera-ture giving maximum affinity	Percentage of common salt giving maxi-mum depth in percentage stated
10% Indigosol Blue AGG Powder	C	20° C.	200
10% Indigosol Blue AZG Powder	C	20° C.	160
10% Indigosol Blue IBC paste	C	20°–90° C.	200
9% Indigosol Brown IBR Powder	A	60°–90° C.	120
10% Indigosol Brown IRRD Powder	C	20° C.	40
2% Indigosol Grey IBL Powder	C	20° C.	160
5% Indigosol O Extra Powder	C	20° C.	200
5% Indigosol O4B Powder	A	30°–40° C.	120
5% Indigosol O6B Powder	A	40° C.	120
6% Indigosol Olive Green IB Powder	A	60° C.	80
5% Indigosol Orange HR Powder	B	20° C.	200
10% Indigosol Pink IR Powder	C	20° C.	200
3% Indigosol Red IFBB Powder	A	50° C.	120
10% Indigosol Scarlet HB Powder	C	20° C.	200
6% Indigosol Violet ABBF Powder	B	20° C.	160
6% Indigosol Violet ARR Powder	B	20° C.	200
10% Indigosol Red Violet IRH Powder	C	20° C.	200
2% Indigosol Golden Yellow IGK Powder	C	20° C.	160
2% Indigosol Golden Yellow IRK Powder	B	20°–40° C.	80
5% Indigosol Yellow V Powder	C	20° C.	200
10% Soledon Black 2B 50 Paste	A	90° C.	80
5% Soledon Blue 4BCS Powder	A	30°–40° C.	120
10% Soledon Blue 4GS Powder	C	20° C.	160
10% Soledon Blue RCS Paste	C	20°–90° C.	200
10% Soledon Dark Blue BS Paste	A	90° C.	40
10% Soledon Dark Blue GS Paste	A	50°–90° C.	80
10% Soledon Dark Blue 2RS Paste	A	90° C.	40
10% Soledon Brown GS Powder	C	20° C.	40
9% Soledon Dark Brown 2RS Powder	A	60°–90° C.	120
6% Soledon Green GS Powder	A	60° C.	80
2% Soledon Grey BS Powder	C	20° C.	160
5% Soledon Indigo LLS Powder	C	20° C.	200
2% Soledon Jade Green XS Paste	A	60° C.	10
5% Soledon Orange RS Powder	B	20° C.	200
10% Soledon Orange 4RS Paste	A	70°–80° C.	120
10% Soledon Pink FFS Powder	C	20° C.	200
4% Soledon Brilliant Purple 2RS Paste	A	50°–60° C.	20
3% Soledon Red 2BS Powder	A	50° C.	120
10% Soledon Red 3BS Powder	C	20° C.	200
10% Soledon Scarlet BS Powder	C	20° C.	200
6% Soledon Violet BS Powder	B	20° C.	160
2% Soledon Golden Yellow GKS Powder	C	20° C.	160
2% Soledon Golden Yellow RKS Powder	B	20°–40° C.	80
2% Soledon Yellow 5GS Powder	C	20° C.	200
5% Soledon Yellow GS Paste	A	50° C.	120

Class A has maximum dyeing affinity   Class C has minimum dyeing affinity
Class B intermediate between A and C

The golden rule of dyeing already enunciated applies with equal force to Soledon and Indigosol dyestuffs, but the limited ranges available make it more difficult to apply.

The dyeing properties of these dyestuffs on variable viscoses approximate to those of the direct cotton dyestuffs, namely,

1. The even dyeing dyestuffs show maximum affinity at 20° C., *e.g.* Indigosol Orange HR, whereas the more uneven dyeing dyestuffs require to be dyed at a higher temperature before they will show maximum affinity, *e.g.* Indigosol Brown IBR.

2. The even dyeing dyestuffs are rapid dyeing, *e.g.* Indigosol Grey IBL, whereas the more uneven dyeing dyestuffs are slower dyeing, *e.g.* Soledon Orange 4RS.

3. The even dyeing dyestuffs show good levelling properties whereas the more uneven dyeing dyestuffs show poor levelling in most cases.

4. There is an increase in the degree of levelling of the uneven dyeing dyestuffs when the dyeing is carried out at a higher temperature.

Even dyeing is judged by the behaviour of the dyestuff to viscose rayon of varying dyeing affinity.

After dyeing the solubilized vat dyestuffs require to be " developed " by which is understood a hydrolysis of the dyestuff by an acid in presence of an oxidizing agent. The speed of hydrolysis depends mainly on the temperature and concentration of the acid in the developing bath, and is only influenced to a certain extent by the amount of oxidizing agent used. Several methods are used for developing, most of which are recommended for printing, but the method chiefly used in dyeing involves the use of sulphuric acid and sodium nitrite. Individual members vary considerably in their ease of development, thus, Indigosol Red IRH is difficult to develop, whilst Soledon Jade Green XS is very easy. The fact that Soledon and Indigosol dyeings fluoresce strongly in ultra-violet light has led the present authors to examine all shades under this light source when development of bulk dyeings is thought to be complete. If the shades fluoresce it is evident that they are not ready for soaping, but require a longer treatment in the developing bath. Certain members, *e.g.* Indigosol Olive Green IB, are prone to over-oxidation, the

shade becoming flatter and yellower, so that as this dyestuff is easy to develop developing should be carried out cold. If over-oxidation has occurred the correct shade can usually be recovered by the addition of 5 per cent. glucose and 2 per cent. soda ash to the soaping bath.

According to Christ (*ibid.*, p. 94) "many Indigosol dyestuffs are sensitive to light which, in most of these cases, affects the ester groups in such a way that the dyes develop prematurely. Results of this kind can have very disagreeable effects in dyeing, *e.g.* the selvedges of cloth exposed to light in jigger dyeing may be darker than the rest of the cloth. A different kind of sensitivity to light is shown by Indigosol Red IFBB. In this case the effects of light rays do not cause a simple splitting of the ester, but a change in the dye molecule itself, whereby the shade becomes bluer. In order to avoid all difficulties which may occur through the action of light in dyeing with Indigosols, it is advisable to darken slightly the room in which they are applied."

APPLICATION TO VEGETABLE FIBRES

The solubilized vat dyestuffs are usually applied to cotton, linen, regenerated cellulose rayons and staple fibre, either in the form of yarn or as piece goods. In general their method of application consists in dyeing in a neutral or faintly alkaline dye-bath in presence of Glauber's or common salt, then developing the dyeing in sulphuric acid and sodium nitrite, followed by rinsing, neutralizing and soaping. Since fairly strong sulphuric acid is used in the developing baths the dye vessels must be constructed of acid-resisting material, which is one of the reasons why these dyestuffs are not more extensively used.

Yarn may be dyed either as hanks, cheeses, or warps in suitable package machines, whilst hanks may also be dyed on sticks in the ordinary hand dyebeck or on machines of the roller type, such as the Gerber machine. The method of dyeing naturally depends upon the type of machine used, on the depth of shade desired, and on the dyestuffs to be used, so that no hard and fast rules can be given. In general the dyebath is set with the dyestuff and Glauber's or common salt, and dyeing continued for $\frac{1}{2}$–$\frac{3}{4}$ hour at ordinary temperatures. For pale shades, on

hard spun yarns and rayon no salt should be added at the commencement of dyeing, and the salt should then be added in small portions during the dyeing. This is particularly essential when dyeing mixtures of, for example, Soledon Jade Green XS and Soledon Yellow GS on viscose rayon, since as shown in the table on p. 219 Soledon Jade Green XS requires much less salt to give maximum value than does Soledon Yellow GS, so that unless the salt is carefully added unlevel dyeings will be obtained owing to the strong affinity of the Soledon Jade Green XS. Similarly the temperature of dyeing has to be regulated. For example, viscose rayon is in general more evenly dyed at 50°–60° C. than by dyeing at ordinary temperatures. Again, although the dyestuff makers recommend development with 20 c.c. sulphuric acid 167° Tw. and 1 grm. sodium nitrite per litre water for $\frac{1}{4}$ hour at 70° C. the quantities of acid and nitrite may successfully be reduced in certain cases and a lower temperature of development employed.

The following example will serve to indicate one method which has proved successful in practice when dyeing 2/60 scoured cotton yarn on the Gerber machine with the following mixing : 0·35 per cent. Indigosol Grey IBL Powder, 0·2 per cent. Soledon Orange 4RS Paste, and 0·02 per cent. Indigosol Brown IRRD Powder, in a yarn to liquor ratio of 1 : 30, using 20 per cent. of common salt. The dyebath is set with the dyestuff and 2 per cent. common salt at 50° C., the yarn dyed for 5 minutes, 4 per cent. salt added, then 6 per cent. salt, and finally 8 per cent. salt added, with 5 minutes' dyeing after each salt addition. Development is then carried out in a yarn to liquor ratio of 1 : 15 with 0·5 grm. sodium nitrite and 1 c.c. sulphuric acid 116° Tw. per 100 c.c. in a 1·5 per cent. salt solution for 15 minutes at 30° C. The yarn is washed free from sulphuric acid and soaped.

Piece goods may be dyed on the jigger, the padding machine, or in the winch machine, the choice of method depending upon the type and weight of material to be dyed, and on the depth of shade desired. Thus the padding method is usually given preference over the jigger for large weights and for medium shades, whilst the winch is most suitable for delicate fabrics such as knitted rayon goods. When dyeing on the jigger half the dyestuff

is added before the first end, and the remainder before the second end. A jigger fitted with squeezing rollers is recommended and four ends are the minimum which should be employed.

Developing may be done on the same jigger, but it is preferable to use two or three jiggers in series, the first jigger being used for dyeing, the second for developing when two ends should be given, and the third for washing, neutralizing and soaping. When using the padding machine the liquor box should be as small as possible, as the smaller the box the quicker is the liquor replenished. The replenishing liquor must always be stronger than the original liquor owing to the substantivity of the dyestuffs ; for dyestuffs with low affinity a 5 per cent. excess and for dyestuffs with a high affinity a 30 per cent. excess of dyestuff over the original strength may be required, whilst rayon and mercerized cotton fabrics require still stronger replenishing liquors. In order to keep the affinity as low as possible padding is best done at 80°–85° C., and the speed of the machine adjusted to the highest rate allowed by the quality of the goods. With most of these dyestuffs development may be carried out in a small volume of liquor, using 20 c.c. sulphuric acid per litre at 60°–70° C., the nitrite being padded on to the cloth with the dyestuff, and the time of development should not be less than 3 seconds. In working without a subsequent air passage the time of development should be increased to 6–8 seconds. (For details of a special developing trough for Indigosols, see Christ, *J.S.D.C.*, 1938, p. 96).

In recent years a one-bath method suitable for pale shades has been developed which may be used on pieces in the winch machine or on yarns with dyestuffs of good substantivity. In this method the dyebath is set with the dyestuff, a protective colloid such as Setamol WS and the sodium nitrite, the dyebath is exhausted as nearly as possible by the addition of salt, and finally the sulphuric acid required for developing is fed into the nearly exhausted dyebath. In the case of Indigosol Blue IBC which has a very low substantivity, an amended one-bath method has been suggested which gives better colour-value and is satisfactory for hank dyeing. This dyestuff is the yellow-coloured tetra ester of leuco-Indanthren Blue BC which on treatment in a weakly acid bath loses two of its ester groups to give the more highly sub-

stantive violet coloured di-ester. This dyestuff is therefore dyed with ammonium acetate, which during dyeing slowly liberates acetic acid, and which also serves to prevent too rapid hydrolysis of the ester by buffering the sulphuric acid which is subsequently formed as dyeing proceeds.

APPLICATION TO ANIMAL FIBRES

The solubilized vat dyestuffs are applied to wool and silk from weakly acid dyebaths, and under these conditions they have in general such a pronounced affinity for these fibres that the dyebath may be completely exhausted. They are seldom used in wool dyeing as other classes of dyestuffs of high fastness properties and lower cost are available, but are occasionally used for dyeing fast to washing shades on silk. On the latter fibre dyeing is begun cold and the temperature slowly raised to 80° C. with suitable additions of acid and Formosul or other formaldehyde hydrosulphites. The dyeings are then developed with bichrome and sulphuric acid either cold, warm or hot, depending on the dyestuffs used. In dyeing it is advisable to select dyestuffs for compound shades which can be oxidized at the same temperature so as to prevent over-oxidation of any one component of the mixing. As compared with the normal method of vat dyeing, the dyeing of silk with these dyestuffs does not damage the fibre to the same extent, due to absence of alkali : their more extensive use is prevented by their higher price.

Section XII.—DYESTUFFS PRODUCED ON THE FIBRE BY OXIDATION OF COAL-TAR PRODUCTS

The dyestuffs described in this section are not dyestuffs in the same sense as those described in the previous sections, but they find a proper place in a book of this nature, since they are produced on the fibre by oxidation of coal-tar products. Some members are of the highest commercial importance, and are characterized by excellent fastness to light and washing. They find their chief application on vegetable fibres, especially in calico printing, and in fur dyeing but are seldom applied to wool and silk. The most important member of this group of dyestuffs is aniline black, which is produced on the fibre by the oxidation of aniline oil or salts by methods described hereafter.

Aniline Black

Aniline Black was first utilized as a lake colour, but it was so radically improved by John Lightfoot of Accrington, whose first patent was E.P. 151 of 1863, that he is generally regarded as the real discoverer of this dyestuff. Lightfoot not only showed the way to use it for cotton printing, the first pieces being printed at the Broad Oak Print Works of Accrington, but also enabled it to be applied for dyeing yarns and piece goods. The methods for the application of aniline black have remained substantially the same as those introduced in the 1860's and 1870's by Lightfoot and others, the only material change being Green's process (*J.S.D.C.*, 1909, pp. 149, 191), which has been little used in this country. On the Continent, however, it has been largely employed. A large amount of research has been done on amines other than aniline but none have given such good results : aminodiphenylamine (Diphenyl Black Base) being the best of these amines.

15   225

The constitution of aniline black was established in 1913 by Green and his collaborators (*J.S.D.C.*, 1913, pp. 105, 108), when it was shown that the oxidation of aniline to aniline black may be assumed to proceed by a series of quinonoid additions according to the following scheme.

$C_6H_5N : C_6H_4 : NH$ (Caro's yellow imide)

$$C_6H_5N : C_6H_4 : NC_6H_4NHC_6H_4NH_2 \xrightarrow{+O} C_6H_5N : C_6H_4 : NC_6H_4N : C_6H_4 : NH$$
(Willstatter's blue imide)   (Willstatters red imide)

$C_6H_5N : C_6H_4 : NC_6H_4N:C_6H_4 : NC_6H_4NC_6H_4NHC_6H_4NHC_6H_4NH_2$ (Emeraldine)

$+ O \downarrow$

$C_6H_5N : C_6H_4 : NC_6H_4N : C_6H_4NC_6H_4NC_6H_4NC_6H_4NHC_6H_4NH_2$ (Nigraniline)
$C_6H_5NH_2$
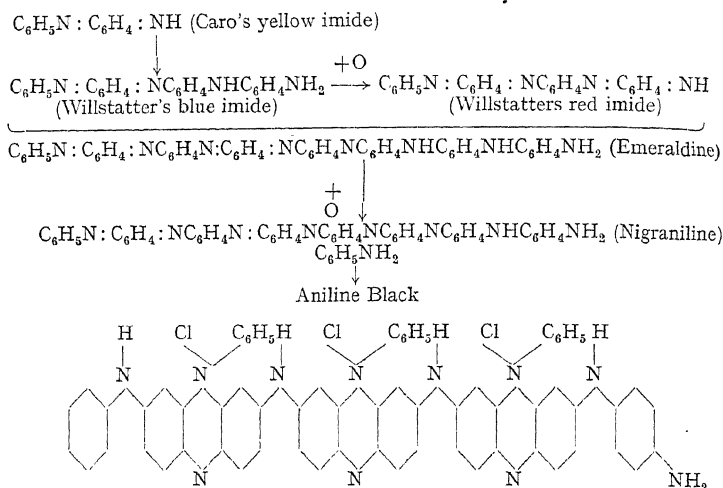
Aniline Black

In practice the formation of aniline black by the acid oxidation of aniline oil proceeds in three well-recognized stages. The first stage results in the formation of emeraldine, of which the free base is blue, but whose acid salts are bottle green, the colour of the cotton as it comes out of the " ager " when being dyed aniline black by the ageing process. The second stage of the oxidation converts the emeraldine into nigraniline, the free base of which is dark blue and the salts blue. Nigraniline is immediately reduced by sulphurous acid to emeraldine, which results in the black being turned green. The final stage of the oxidation converts the nigraniline into the ungreenable aniline black, so-called because it is not reduced by sulphurous acid to emeraldine : when reduced by hydrosulphite ungreenable aniline black changes to brown, which on exposure to the atmosphere is reconverted into black.

The above reactions of nigraniline and ungreenable aniline black has given rise to the terms greenable and ungreenable black. The way in which an aniline black behaves to sulphurous acid is a test as to whether the aniline black has been fully developed ; if

it turns green the black still contains nigraniline, and has not been fully converted.   One bath aniline blacks are turned green, but properly dyed aged and steam aniline blacks are ungreenable. It is, therefore, a common trade test to submit aniline blacks to a sulphurous acid treatment in order to determine whether it will turn green or not, and an aniline black dyer is judged successful or otherwise according to the result of this test.   For this purpose the following reagent has been recommended : 2·0 c.c. sodium bisulphite 70° Tw., 20 c.c. hydrochloric acid 34° Tw., 500 c.c. water.   The material is worked 10 minutes cold in this solution, washed, dried, and compared with an untreated pattern.

Aniline black is comparable with the vat blacks in its fastness to light, washing and bleaching (single bath aniline black is not fast to bleaching), and is less expensive to dye than are vat blacks. Like sulphur blacks, which however will not stand bleaching, aniline black is extremely fast to light.   Prolonged comparative exposures of a Prussiate aniline black and a sulphur black have shown that there is practically nothing to choose between the two after 6 months.   Sulphur black is, however, much more quickly dyed than aniline black, but the possible tendering of cellulose by sulphur black is a disadvantage as compared with aniline black. The fibre is usually tendered to a certain extent when dyed with aniline black, but the tendering is definite and not progressive, whereas sulphur black tendering once it starts is progressive.

Large quantities of cotton yarn and pieces are dyed with aniline black, but it is rarely dyed on loose cotton except on a sulphur black bottom (see p. 167).   The cotton must be thoroughly cleaned by a preliminary boiling out with alkali before being dyed and, since free mineral acid is necessary for the formation of aniline black, the cotton must be washed free from alkali.

Aniline black is dyed on the commercial scale by three distinct processes, viz :

    1. Single-bath aniline black.

    2. Aged aniline black.

    3. Steam aniline black.

Before considering the above three processes it is necessary to explain that the recipes for aniline black are legion, therefore the recipes given hereafter are capable of being varied within wide limits.

The successful dyeing of aniline black on the big scale calls for great skill and constant attention on the part of the dyer in order to obtain satisfactory results without tendering the material. Since aniline black requires the presence of mineral acid for its production, it will readily be understood that there is always a danger of tendering. Local conditions in processes 2 and 3 play a very important part, so that a recipe which is satisfactory in one dyehouse may be unsatisfactory in another dyehouse. Recipes have to be altered to meet these conditions, which explains the variation to be found.

1. **Single-bath Aniline Black.**—This process is the easiest to carry out, but gives the least satisfactory results. Blacks dyed this way are turned green by sulphurous acid, they are not fast to chlorine and rub badly, but they are fast to light and milling. Despite these drawbacks large quantities are dyed on yarn—formerly for the Eastern export trade ; it is but rarely dyed on loose cotton or piece goods.

The shade produced is controlled by three factors :

1. Proportion of liquor to material.
2. The temperature to which the dyebath is raised.
3. The after-treatment to which it is submitted.

The higher the proportion of liquor to material, the more aniline oil is required for the same depth of shade. The following recipe is a typical one for a single-bath aniline black.

For 100 lb. cotton yarn.

> 10 lb. aniline oil
> 10 lb. spirits of salts
> 10 lb. iron liquor
> 10 lb. D.O.V.
> 20 lb. sodium bichromate
> 120 gallons water

The bath is made up as follows : the bichromate is dissolved in hot water, added to the cold dyeliquor, the iron liquor and then the D.O.V. added and the liquor well stirred. The aniline oil and spirits of salts are mixed together with a little water to keep the fumes down, and the mixture stirred until the aniline is completely dissolved. This operation is best carried out in the open air because the fumes are poisonous and their inhalation should be avoided. The solution of aniline hydrochloride is added to the dyeliquor immediately before the yarn is

entered, because as soon as it is added, the formation of aniline black commences.   After the yarn is entered it is worked for 1 hour cold, then the liquor raised slowly to the boil, lifted out and washed off thoroughly to remove all acid.   The temperature to which the liquor is heated plays an important part in the ultimate shade of black obtained.   If the temperature is only raised to 60° C. the shade is much redder than if it is raised to the boil, but the material will be dustier.   After washing off, the yarn is either soaped or treated with an emulsion of oil, which improves the shade considerably.   Alkali reddens the shade, so that unless a bronzy shade is required, it should not be used in after-treating aniline black.   The higher temperature gives the dustier shade.

Large quantities of aniline black on cotton yarn for exporting to the East have been dyed by the following recipes :

Aniline Black Bronze Shade :   For 100 lb. cotton yarn

4½ lb. aniline oil	4½ lb. iron liquor
4½ lb. spirits of salts	9 lb. bichromate
4½ lb. D.O V.	120 gallons of water

The yarn is worked 1 hour cold and the temperature of the liquor raised to 60° C. in ½ hour, washed off and then soaped for ½ hour at 60° C. with 10 per cent. soap and ½ per cent. soda ash.

Aniline Black Dead Shade :   For 100 lb. cotton yarn

5 lb. aniline oil	5 lb. iron liquor
5 lb. spirits of salts	10 lb. bichromate
5 lb. D.O.V.	120 gallons water

The yarn is worked 1 hour cold and the temperature of the liquor raised to the boil in ½ hour, washed off and then soaped for ½ hour at 60° C. with 10 per cent. soap.   The dead shade will always be found to be much dustier and dirtier than the bronze shade.

2. **Aged Aniline Black.**—This is the most widely used of the three processes for dyeing, as distinct from printing, and gives an excellent shade of black, which is fast to light, washing, and bleaching and is not turned green by sulphurous acid.

The principle of this process consists in impregnating the cotton with aniline salts, an oxidizing agent, an oxygen carrier and an acid-producing substance.   The oxidizing agent which is almost universally used is sodium chlorate, and is preferred to the potassium salt owing to its greater solubility.   The oxygen carriers

employed are copper sulphide, copper sulphate, and vanadium chloride. The acid-producing substance used is ammonium chloride, and its function is by its hygroscopicity and dissociation at the temperature of the ager to start the reaction. Wooden or stone vessels are used throughout ; no metal must be present.

The following recipes are only given as typical ones and may require to be varied to suit local conditions.

Aniline Black with Copper sulphate : this recipe gives a fast to bleaching aniline black on yarn.

Dissolve :

60 parts aniline salt in 320 parts water, and neutralize, if necessary, by addition of aniline oil
$2\frac{3}{4}$ parts copper sulphate in 50 parts water
19 parts sodium chlorate in 37 parts water
2 parts ammonium chloride in 12 parts water
24 parts aluminium acetate 15° Tw.

Mix together when the resulting liquor will stand at about 12° Tw. The yarn is padded in this liquor 2 lb. at a time and wrung out so that it holds its own weight of liquor. It is then dried in a stove at 35° C. on sticks which have been saturated with the above liquor in order to avoid stick marks ; the yarn is turned every 2 hours (the workman must have dry hands, wet hands will make finger marks) ; dry steam is then let into the stove till the dry bulb shows 35° C. and the wet bulb shows 30° C. The yarn is left at this temperature for 6 hours, by which time it should have turned to a dark bottle green. It is then removed from the stove and chromed for $\frac{1}{4}$ hour at 80° C. with 4 per cent. bichromate and 1 per cent. sulphuric acid, which turns the yarn to a jet black, thoroughly washed off and finally soaped $\frac{1}{4}$ hour at 80° C. It has been shown that it is necessary to have free aniline present in the last stage of oxidation in order to produce ungreenable aniline black, so that aniline salts are sometimes added to the chrome bath.

Aniline Black with Copper sulphide. Copper sulphide in the form of a paste is used as the oxygen carrier, and is made by the double decomposition of copper sulphate and sodium sulphide as follows : $37\frac{1}{2}$ parts copper sulphate are dissolved in 150 parts water, to which is added 39 parts sodium sulphide crystals in 100 parts water, the copper sulphide filtered off and the paste pressed till it yields 54 parts, in which concentration it is used.

15 parts aniline salts made neutral with aniline oil
5 parts copper sulphide paste
5 parts sodium chlorate
75 parts water
___
100

The strength of the padding liquor is determined by the quality of the cloth.   The cloth should be squeezed so that it retains its own weight of padding liquor, dried, given a 3 minutes' passage through the ager at 60° C. then chromed and soaped.   The black may also be developed by hanging, which naturally takes much longer, but the danger of tendering is greatly minimized.

Aniline Black with Vanadium Chloride :

8   parts aniline salts
1½ parts aniline oil
4   parts sodium chlorate
5   c.c. vanadium chloride solution
81½ parts water
___
100

The cloth is padded with the above, dried and developed by a 2 minutes' passage through the ager at 95° C. or by hanging.   A subsequent treatment with bichromate is not necessary.

Vanadium chloride solution is made as follows : 8 grs. ammonium vanadate are dissolved in 40 grs. hydrochloric acid and 80 c.c. water, then reduced by warming with 10 grs. glycerol till the solution turns blue, and finally diluted with water to 2 litres.

The amount of vanadium required is extraordinarily small ; compared with copper sulphide it has the drawback, however, that, being soluble, the padding liquor begins to oxidize much more quickly and, therefore, is not so stable.   Copper is, therefore, much more largely used than vanadium.

Green's Aniline Black Process : In 1907 Green took out a patent by which it was claimed that it is possible to avoid tendering of the fibre.   The patent is E.P. 16189 of 1907, to which the reader is referred if details are required.   As far as the authors' knowledge goes, it has not been adopted commercially in Great Britain.

3. **Steam Aniline Black.**—This process for the production of aniline black is more largely used in calico printing than in dyeing, though the black is reputed to be less greenable than the " aged " black, whilst the danger of tendering the fabric is also

less. The padding liquor may also be kept longer without formation of aniline black. As the black does not develop as far in the steaming as an aged black it, therefore, requires to be thoroughly after-chromed. The following is a typical recipe :

  I. 84 parts aniline salt neutralized, if necessary, with aniline oil,
     dissolved in 300 parts water.
 II. 49 parts yellow prussiate of potash dissolved in 300 parts water.
III. 27 parts sodium chlorate dissolved in 300 parts water.

Each ingredient is dissolved separately and when required mixed together in equal portions. The material is padded, dried, steamed 2–3 minutes, then chromed at 50° C. with ½ lb. bichromate per 10 gallons.

Diphenyl Black.—This product, introduced by Meister, Lucius, and Brüning in 1892 (D.R.P. 134,559), was marketed as Diphenyl Black base and consisted of amino-diphenylamine. A mixture of 1 part amino-diphenylamine and 3 parts of aniline oil was also marketed as Diphenyl Black Oil DO. The advantages claimed for this black over aniline black were :

  1. The black was absolutely ungreenable.
  2. The fibre was not tendered in the least degree owing to the absence of mineral acid, whereas aniline black requires mineral acid for its development.

Owing to the considerably higher price of the product as compared with aniline oil, its introduction has not proved a serious rival to aniline black.

The following recipe for piece dyeing is given by the makers :

A Diphenyl Black Base

Standard Solution A
 60 parts tragacanth solution 1 : 10
 75 parts water
 40 parts Diphenyl Black base dissolved in
 50 parts lactic acid 50 per cent., and
130 parts acetic acid 40 per cent., are stirred into the
     tragacanth after cooling and made up to
500 parts with water

Standard Solution B
 25 parts aluminium chloride 52° Tw.
 25 parts chromium chloride 52° Tw.
  4 parts copper chloride 76° Tw.
340 parts water are mixed with
 30 parts sodium chlorate dissolved in
 60 parts hot water and
 10 parts turpentine

Equal portions of A and B are mixed together. The standard solutions are stable, but no more of the two solutions should be

mixed than can be used each day. The cloth is padded to hold its own weight of liquor, dried, steamed 2 minutes at 100° C., washed and soaped at 60° C. ; chroming is detrimental as it depreciates the shade.

It is reported that Diphenyl Black is extensively used in America for printing on cellulose acetate rayon.

Aniline Black on Wool and Silk.—Aniline black does not develop on wool and silk like it does on vegetable fibres due to the reducing action of the fibre. The production of aniline black on wool has attracted many investigators—notably Kallab—but it has never been made a commercial success. Indeed, the authors can see no place for aniline black—as such—on wool, remembering the very satisfactory range of fast chrome blacks which are available, and which practically meet all the requirements of the wool dyer.

There is, however, one special application to wool and silk which should be included here. It is confined to silk and mohair pile fabrics, and is used for producing chinchilla and black shades with white tips. This is carried out as follows : the material is worked cold for 15 minutes in a solution containing 5 parts potassium permanganate and 7 parts zinc or magnesium sulphate in 1,000 parts water, the temperature raised to 50° C. in $\frac{1}{2}$ hour, washed off and dried. The object of the zinc or magnesium sulphate is immediately to neutralize the caustic alkali which is liberated by the permanganate of potash, and so prevent it damaging the wool or silk. This bath dyes the fibre a dark brown due to the precipitation of oxides of manganese on the fibre.

In order to produce white tips the oxides of manganese are discharged by what is termed a " cutting liquor " consisting of 3 quarts hydrogen peroxide, 1 pint acetic acid and 1 oz. oxalic acid dissolved in 1 pint water. This is suitably thickened to prevent it running on the fibre when brushed on. Girls specially trained to the work brush the cutting liquor on in any desired design. After the fabric has dried the black is developed by working for 10 minutes cold in a bath containing 1,000 parts water, 5 parts aniline oil and 5 parts D.O.V.

The fabric is not black when it comes out of the bath, but the development of the black is completed by soaping, with the

addition of a little ammonia at 40° C. Wherever the cutting liquor has been brushed on the shade will not have developed, so that the fibre remains white.

Chinchilla effects are produced on exactly the same lines by reducing the quantities of permanganate and aniline oil employed.

Paramine Brown, Fuscamine and Ortamine Browns.— These browns are produced on the fibre in an analogous way to aniline black from :

Paramine (paraphenylene diamine), D.R.P. 176062, 1904.

Fuscamine G (meta-amido-phenol), D.R.P. 210643, 1908.

Ortamine D (ortho-di-anisidine), D.R.P. 250466, 261871.

which were put upon the market as a result of the work of Henri Schmid, of Mulhouse, who developed the recipes given below. It will naturally be thought that this would have been carried out earlier, but all the results obtained by using the hydrochlorides in similar manner to aniline salts were not practicable, due to the tendering of the fibre, though the shades obtained were particularly fast.

The following processes yield shades fast to light and washing, whilst they have the additional advantage of being easily discharged which makes them of special advantage in calico printing. Paramine gives a red chocolate brown, whilst fuscamine and ortamine give yellow-brown and biscuit shades.

Padding liquors are made up according to the following recipes :

Paramine Brown.—20 grs. paraphenylene diamine are dissolved in 250 c.c. hot water and then diluted with 450 c.c. cold water. $1\frac{1}{2}$ grs. Rongalite C are now added to prevent oxidation of the paraphenylene diamine and 20 grs. sodium chlorate dissolved in 50 c.c. water, and 30 c.c. tartar emetic glycerine solution are added. This is then diluted to 1 litre with cold water, filtered and 0·015 gr. ammonium vandate added just before use.

The tartar emetic glycerine solution increases the stability of the above padding liquor, and is made up from 40 grs. tartar emetic, 340 grs. glycerine and 620 c.c. hot water.

Fuscamine Brown.—20 grs. meta-amino phenol are dissolved in 20 grs. hydrochloric acid 30° Tw. and diluted to 400 c.c. with water. 25 gms. sodium chlorate in 100 c.c. water are then added,

followed by 5 grs. potassium ferrocyanide in 100 c.c. water and the whole diluted to 1 litre.

Ortamine Brown.—28 grs. of ortho-dianisidine are pasted with water, 7 grs. hydrochloric acid 30° Tw. and 20 grs. formic acid 90° added, the mixture warmed till dissolved, cooled, 20–25 grs. sodium chlorate added, the solution diluted to a litre and filtered. 0·4–0·6 per cent. potassium ferrocyanide or ferrous sulphate is then added as catalyst.

The material is padded with any of the above solutions, dried at 100°–120° F., steamed 3–5 minutes, soaped, washed, and dried.

The three products are miscible one with another, which enables a large range of brown and biscuit shades to be obtained.

FUR DYEING

This is a special branch of dyeing which falls in this section, since furs are largely dyed by the oxidation of coal tar products on the fibre. The three bases which are most commonly used for fur dyeing are paraphenylene diamine, para-amid-phenol, and ortho-amino-phenol ; pyrogallic acid is also used to a lesser extent. Paraphenylene diamine is the most important product for black dyeing.

Owing to pelts being so sensitive to heat, the ordinary processes of dyeing are inapplicable ; therefore, fur dyeing is carried out cold in order to preserve the pelts. The products enumerated above are put on the market under several fancy names, such as Ursol, Nako, Furrol, etc.

The dyeing of furs is a difficult branch of dyeing which requires great skill, coupled with experience and knowledge of the furs. The preliminary process in fur dyeing is technically called " killing," which is in reality a degreasing operation, so that the individual fibres will be in a fit condition to absorb the mordants and dyestuffs. The chemicals used for this purpose are lime and soda, the former g ving the better result ; the skins are soaked for 2 hours in a cold bath containing 1 lb. lime to 10 gallons water. They are then thoroughly washed to remove all lime previous to mordanting.

From the dyeing point of view furs may be roughly divided into two classes, viz :

1. Sheepskin, Persian goat, kid, kid-cross, schmasche, lamb, and allied skins.

2. Rabbit, hare, fox, opossum, musk, goat (long haired as distinct from the Persian goat) and allied skins.

The distinction between these two classes is that the individual fibres of the former have a much greater absorbing capacity or penetrability than the latter.

The principle of this method of fur dyeing is the oxidation on the fibre of the bases enumerated above. This is carried out by first mordanting the skins with an oxidizing agent. Bichromate, copper sulphate, and iron salts are the three chief mordants used. Light shades are dyed without previous mordanting, but dark shades are usually first mordanted. Hydrogen peroxide is the oxidizing agent used in the dyebath itself, and is added to the dyebath after the fibre has become thoroughly saturated with the base.

Paraphenylene diamine is the base most commonly used in fur dyeing, but the workpeople must be well protected from it or they are liable to contract skin diseases and blood poisoning.

Black with Paraphenylene Diamine.—A 1 per cent. solution of paraphenylene diamine is made up and acidified with acetic acid. The furs are worked in this at 100° F. (40° C.) until they are thoroughly saturated, then 5 c.c. hydrogen peroxide (10 vol.) for every gram of paraphenylene diamine is added, and the temperature allowed to fall gradually to normal. The furs gradually develop to a full black, providing the bath is kept on the acid side with acetic acid throughout, a full black being developed in 8–10 hours.

A modified recipe is as follows :

5 lb. paraphenylene diamine is dissolved in boiling water, made up to $7\frac{1}{2}$ gallons with cold water, slightly acidified with acetic acid, cooled and $2\frac{1}{2}$ gallons hydrogen peroxide (10 vol.) added. If this is brushed on and allowed to stand, it produces a black.

Brown with Paraphenylene Diamine.—Proceed as above except that the bath is made alkaline with soda ash, when a brown instead of a black is obtained.

Fur dyeing has for its chief object the colouring of inferior skins to look like the more expensive and rare skins, such as sable, etc. In order to produce the markings of the natural furs the solution of the various bases mixed with hydrogen peroxide, already described, are brushed on in as close an imitation as possible of the genuine article.

A recent development in fur-dressing has been made by the use of the chrome tanning process for the pelts, so that the furs may be dyed at a higher temperature (55°–60° C.), thus permitting the use of selected coal-tar dyestuffs to give shades which do not occur in natural furs but find a use in toning with current fashion ensembles for trimming and decorative purposes. Mr. Maskell has introduced a process to which the name of "Strathanizing" has been given. This process has been applied mainly to mole-skins; the pelts are first chrome tanned and then dyed to the desired tone at higher temperatures with coal-tar dyestuffs. Incidentally the claim is made for this process that there is no danger of dermatitis arising from the use of furs so treated. Whilst it is correct to say that the dermatitis risk is less than with furs dyed with bases oxidized on the fibre there still remains the normal risk of claims arising from persons idiosyncratic to a particular pelt. After being dyed furs are usually cleaned by drumming in cork sawdust.

A method for dyeing furs on chrome tanned pelts up to 55°–60° C. has also been patented by Mendoza, White, and the I.C.I. (E.P. 475966).

(Modern fur dyeing has been reviewed by T. R. V. Parkin in the Jubilee issue of the *Journal of the Society of Dyers and Colourists* 1934, p. 203 ; see also " Fur Dyeing," E. Beeley, *J.S.D.C.*, 1933, p. 218.)

Section XIII.—THE DYEING OF RAYONS

THE term " artificial silk," which was formerly used to avoid any possible confusion with natural silk in the mind of the buying public has been replaced in this country and in the U.S.A. by the name " rayon," and in Germany by the name " Glanzstoff." The name indicates that these fibres are not natural silk substitutes, but are individual textile materials with distinctive and desirable properties of their own.

In the earlier stages of their development the dyeing of regenerated cellulose rayons was usually dismissed in a few sentences indicating that they could be dyed like cotton. Such a statement is an economy of the truth because, though true in principle, the details vary considerably. Owing to the fact that problems occur in the dyeing of rayons which never occur in the cotton dyehouse it has been thought advisable to devote a complete section to the dyeing of these fibres so that this very difficult branch of dyeing may be adequately treated.

From the dyeing point of view, commercial rayons may be divided into two groups :

1. Nitro-cellulose ; cuprammonium, and viscose.

2. Cellulose acetate.

Of these nitro-cellulose rayon no longer possesses any commercial importance, whilst the relative importance of the other rayons is shown by the following world production figures for 1937 (*Silk Journal* and *Rayon World*, 1938, p. 26) :

Viscose Rayon	..	..	..	.. 86·8 per cent.
Cellulose acetate rayon	..	..	.. 8·9	,,
Cuprammonium rayon	..	..	.. 4·3	,,

the total weight being 1,159,555,000 lb.

In 1940 the world production of rayon was 2,380,810,000 lb., of which 1,143,960,000 lb. was rayon filament yarn and 1,236,850,000 lb. rayon staple fibre. This is noteworthy as being the first time that the production of staple fibre has exceeded that of rayon filament yarn.

The two groups are distinct in their dyeing properties, requiring different dyestuffs and methods of application. For the first group those classes of dyestuffs which are suitable for cotton are used, although this statement requires many reservations in actual practice. The early days of the successful commercial production of cellulose acetate yarn were beset with grave difficulties in its dyeing as it possessed no affinity for most of the dyestuffs then available. This necessitated the building up of a special dyeing technique, coupled with the manufacture of dyestuffs exclusively for the dyeing of cellulose acetate, which is dealt with in detail later in this section.

Continuous filament rayons are usually dyed in skein or fabric form, but the dyeing of continuous filament viscose rayon in package form is now in course of development ; the obvious form of package being the cake as produced in the Topham box. There is little doubt that, with the exception of twist yarns, cake dyeing will eventually displace skein dyeing. Each method of dyeing has its own advantages and disadvantages. The skein dyer is able to alleviate any variation in shade occurring in the skeins by sorting them subsequent to dyeing, whereas once rayons of varying dyeing affinity are woven up the piece dyer is helpless, but can reduce his difficulty by intelligent choice of available dyestuffs. On the other hand, the piece dyer has the advantage in manipulation, as when dyeing on the jigger, winch, or pad, the fabric goes through the dyeliquor in open width and in a single layer, but when rayon skeins are entered into the dyeliquor some time elapses before the yarn is completely turned in the dyeliquor, during which time the outside threads are absorbing more dyestuff than the inside threads, whilst there is the additional danger of the skeins being " ended " (*i.e.* dyed more heavily at one end than at the other). Again, although the cake dyer is able to deliver yarn in superior condition for winding to that of skein dyed yarn, the fact that a rayon cake when wet becomes swollen presents serious penetration difficulties, whilst its excellent filtering properties demand excellent water and very soluble dyestuffs. Again, sorting difficulties are experienced if cake dyed yarns are required for weft, since it is impossible to sort cakes or to make an accurate sorting of yarn when wound on to pirns.

There are two factors in the handling of rayon which demand

special attention from the dyer as compared with the handling of cotton, viz. :

1. The affinity of rayon for dyestuffs is much greater than that of cotton.
2. Rayon, both in the dry and more particularly in the wet state, will not withstand the same degree of handling which may be given to cotton without detriment.

These two factors create difficulties in manipulation which require the very careful attention of the dyer. Rayon must not be subjected to any strain or friction during dyeing. Strain produces bright places in the final fabric, whilst friction breaks individual filaments resulting in a hairiness of the threads which, if aggravated, causes them to become matted with adjacent threads. This produces trouble in winding and in all subsequent manufacturing processes.

Careful and continuous attention must be paid to the dyeing apparatus to see that it is free from roughness. To obviate roughness, Monel metal and stainless steel are being increasingly adopted as these take a fine polished surface and have the advantage over copper that they have not the same deleterious effect on the shade of many dyestuffs. In addition they may be used for vat and sulphur dyestuffs which cannot be used in the presence of copper. Enamelled metal utensils will also be found quite satisfactory though they have a definite limit in size, and their cost is usually greater than that of corresponding wooden vats lined with Monel metal or stainless steel. Hard rubber may also be used, but this has the disadvantage that it tends to develop a roughened surface which may be likened to a cat's tongue.

It will be readily understood that the strong affinity of rayon for dyestuffs requires special manipulative precautions to obtain level shades. Skeins are either dyed by hand on sticks or on machines. When dyeing on sticks by hand, unless the skeins are turned quickly there is a great danger of ended skeins ; more labour must, therefore, be employed in order to achieve this, so that four men instead of two should be employed for a batch of 100 lb. while even more men will be found advantageous for the first three turns. Yarn sticks made from steel tubes covered with hard rubber, or made from Monel metal or stainless steel without a rubber covering will be found most suitable since the smooth

surface does not fret the rayon, while they are easily cleaned when changing from one shade to another. Bamboo canes are also largely used though these are very liable to split under hard usage. Turning the yarn by means of the double stick principle will be found to reduce direct handling of the yarn. Discretion must be employed in the rapid turning and travelling of the yarn, or trouble will be experienced in the subsequent winding. Correct manipulative control during dyeing may be more readily obtained by the use of dyeing machines than may be obtained by hand labour. A type of machine which is largely used is the rotating roller machine (p. 64) which was originally designed for the dyeing of natural silk.

The Klauder-Weldon machine is largely used in the United States and Canada, and to a smaller extent in Great Britain ; the authors consider it unsuitable owing to the drag on the yarn when the stick is turned.

It will be found advisable not to overcrowd the rayon in the dyebath, so that a larger volume of dyeliquor is usually taken than in the dyeing of cotton.

The use of soft water is strongly to be recommended for rayon dyeing because soap is an ideal assistant—not only from the point of view of level dyeing, but also as a lubricant. It minimizes friction between the individual threads as well as with the sides of the cistern, etc. In the knitting trade a soft yarn which will slip over the needles is required. This desired softness is obtained by the use of soap in a soft water ; if hard water is used there is a great danger of the formation of lime soaps which would make the rayon sticky and tend to blind it. With such waters the addition to the dyebath of auxiliary products such as the Lissapols, Igepons, Gardinols, or Calgon, etc., prevents the precipitation of these lime soaps and their attachment to the rayon.

If the yarn has to be subsequently sized, no soap or oil may be left on the fibre because this would prevent the size from being absorbed to the extent requisite for a good weaving yarn. The use of metallic salts for the after-treatment of dyestuffs should also be reduced to a minimum, because yarn so treated will never wind well, whilst the treatment has a waterproofing action on the yarn which makes it resist subsequent sizing.

It is hardly necessary to state that rayon yarn should never be

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wrung out like a cotton hank. Delicate multi-filament yarns should be wrapped in cloths after dyeing, previous to hydro-extracting, to prevent damage to the filaments during this process. It is worth noting that discretion should be used in applying the brake to the cage, because if the brake is put on too suddenly there is a danger of the yarn moving in the cage, thereby tearing the outside threads by the perforations of the cage. A good plan is to cut off the current a few minutes before it is necessary to apply the brake so that the cage can slow down somewhat.

Drying should be carried out at as low a temperature as local conditions will allow ; 50° C. is a very suitable temperature, although room temperature gives the best results if floor space, time and conditions permit this to be used. If drying is done by continuous circulation of air care must be taken to avoid too rapid a current, because this has a tendency to open the filaments. After hanging on the stove poles any twisted skeins should be carefully straightened to allow of uniform drying. This is very important, as if partially dry yarn is shaken out on a straightening peg prior to " dolling " there is a danger that such yarn will produce bright picks when the yarn is subsequently woven. Yarn should always be delivered dry to the winding frame because it is more liable to hold up on the swift if not properly dry. Good winding yarn is of the highest importance because a bad winding yarn—apart from the prevalence of knots due to breakages—will give increasing trouble in every subsequent stage of manufacture.

It may here be interpolated with regard to the winding of dyed yarn that a well-dyed 4 oz. skein (with direct cotton dye-stuffs) should run off within 5 minutes of an undyed skein of the same denier. Good winding yarn will not be obtained if the yarn has been in actual process more than 45 or 60 minutes at the outside, and it may usually be expected that a dyed yarn which has been redyed for off-shade or any other reason will take twice as long to wind as a normally dyed yarn. Yarn dyed by long processes as must necessarily be employed for developed, basic (on a mordant), or vat dyestuffs, must always be expected to wind poorly compared with yarn dyed with direct cotton dye-stuffs. Again, shades after-treated with metallic salts usually wind poorly because yarn so treated will often be found to be sticky and hold up the swifts. When handling yarn, extreme

care must be taken to avoid getting hold of a few threads only or catching them on to buttons, etc., because this displaces the lay of the skein and causes tight and slack threads. A great proportion of stoppages when winding off a skein will be found to be due to these slack threads or loops locking round other threads or even catching on one of the arms of the swift. Lacings should be free and not matted. There is a curious divergence between the United States and Britain on the material of these lacings, as in the United States cotton lacings are preferred by the dyers, whilst in Britain rayon lacings are used.

It is frequently demanded that yarn should be scrooped in imitation of real silk. In this connection it must again be mentioned that a scrooped yarn will not wind as well as an ordinary yarn. The following recipe will be found to give a good scroop.

After dyeing and hydro-extracting work with 10 per cent. soap for 20 minutes at 60° C. hydro-extract and work for 20 minutes at ordinary temperature in a bath containing :

> 12 oz. Tartaric acid
> 8 oz. Gelatine } per 10 gallons.
> 4 oz. Formaldehyde (40 per cent).

Hydro-extract and dry without rinsing. Recently lactic acid has had a vogue for scrooping, but in no case is a permanent scroop obtained.

The dyeing of viscose rayon in the cake form, as obtained in the Topham centrifugal box during the manufacture of viscose rayon is the form in which such yarns will be dyed in the future owing to the better windability and quality of the yarn which reflects itself throughout all subsequent processing, thereby reducing costs.

Many machines have been developed and marketed for the dyeing of viscose cakes, whilst the patent files indicate the interest which is being taken in this new branch of dyeing. Two general principles are being exploited. Adaptation of the principle employed in standard dual flow enclosed cheese dyeing machines with special perforated holders adapted to the form of the cake. Some build the cakes in a vertical position, others build the cakes in a horizontal position. The other principle uses the uniflow pack machine with containers which may be whizzed without

unloading ; this latter obviates the use of special formers and is, therefore, more adaptable to varying sizes of cakes.

For the dyeing of fabrics, both the jigger and padding machines are used with the tension reduced to a minimum by the use of ball bearings, the padding machine being particularly suitable for the dyeing of combinations of hard-twisted cotton and rayon. Knitted fabrics and other fabrics which are not injured by creasing are dyed in the rope form on the winch machine, in which the winch should be fitted as near to the level of the liquor as possible so as to prevent undue drag on the fabric. The drying of fabrics after dyeing has an important bearing on the finish, especially when a soft handle is required. A hydro-extractor may be used to partially dry loose-dyed cloths, but for fabrics that should be kept at width it is advisable to have a machine on which the roll may be revolved at high speed so as to throw out as much superfluous moisture as possible or the water may be sucked out of the fabric by vacuum. The pieces may be dried in a loop drier or, alternatively, on a cell drier consisting of flat steam-heated cells arranged in tiers with free running rollers at the end of the cells to allow the fabric to pass through at a minimum tension. Ordinary drying cans may be used for some cloths, but they are not desirable where a full handle is required. Fabrics with a rayon weft must not be subjected to too great lateral tension in the tentering machine, as otherwise the weft threads will be stretched too much and partially torn.

Staple fibre may be dyed in the form of loose cut lengths, sliver, roving bobbins, cheeses, cones, skeins, warps, hose, knitted fabrics and pieces. When dealing with loose cut lengths or sliver it must be remembered that staple fibre swells when wet and packs very solid. It follows, therefore, that it is not advisable to pack the machines with the same full charge as is usual with cotton or wool, but to allow the staple fibre room in which to swell. Sliver may be reeled into hanks and then packed into the machine which makes for convenience in handling. Chain warps may be dyed in machines of the Obermaier type (p. 74), which ensures thorough penetration of the threads and allows of hydro-extraction in the container. Since the warp is not subsequently passed through nip rollers there is no danger of cutting ends as may happen when the lace bands or cut marks pass through the nip. When dyeing

vat dyestuffs the warps are repacked once, but when dyeing direct cotton dyestuffs it is not necessary to repack. The container should be of the type which may be transferred to a hydro-extractor for whizzing purposes. If the warps are dyed on the ordinary warp dyeing machine the nip rollers should be of soft rubber, and great care should be exercised when the leasing bands and cut marks pass through the rollers or ends are very liable to be cut.

Roving bobbins, and cheeses call for no special comment if suitable dyestuffs are chosen, but the packages should be wound sufficiently soft to facilitate penetration.

Skeins may be dyed on the rotating roller type of machine (p. 64) or in machines of the Obermaier type ; they present no difficulty except that on the rotating roller machine the skeins sometimes show a tendency to float on the liquor, in which case the addition of soap should be controlled until the skeins are sinking normally.

In handling knitted fabric made from 100 per cent. staple fibre it is essential to use minimum tension during wet treatment, more particularly on the winch. Failure to guard against tension will result in the impoverishment of the handle of the finished goods. Dyers of both knitted and woven fabrics have observed the tendency of staple fibre to give rise to swealing or colour migration. Direct cotton colours possessing poor wet fastness are prone to give rise to this fault on fabrics, and when dyestuffs of poor wet fastness cannot be avoided one should use a minimum quantity of dyestuff and dye it to complete exhaustion if possible, whilst it is obvious that the goods should not be left lying about in the wet condition but dried immediately.

Piece goods are handled on the winch in rope form or on the jigger. If a clear face is required it will be necessary to singe. Crêpe fabrics containing acetate, viscose, or cotton warps with staple fibre crêpe wefts are handled by similar methods to cotton crêpe fabrics of similar construction. The usual precautions must be taken to prevent cracked and " rained on " effects by obtaining maximum contraction in the crêping process before dyeing.

The drying of staple fibre requires to be most carefully carried out and not in a haphazard manner. It is essential that it should be dried at a low temperature, *e.g.* trouble in the subsequent

dressing of staple fibre warps has proved to be entirely due to over-drying, with the result that ends snapped on the dressing frame. With pieces minimum tension must be used. Grey warp shrinkage is an important factor, particularly in regard to 100 per cent. staple fibre fabrics; at least 4 per cent. is recommended which gives a considerably better general appearance free from open effects, whereas if 2 per cent. warp shrinkage only is allowed the fabrics have an open and papery handle.

Continuous drying gives very good results, and Palmer finishing is also to be recommended, provided the drum temperatures are not too high. In addition to the use of suitable percentages of softeners the best results as regards handle are always obtained when the pieces contain their normal moisture content.

DYEING

In the dyeing of rayon the following classes of dyestuffs are used :

1. Direct cotton dyestuffs.
2. Basic dyestuffs.
3. Sulphur dyestuffs.
4. Azoic dyestuffs.
5. Vat dyestuffs.

Rayon may be dyed in all the varied fastnesses which may be required for any textile purpose, the chief of which are enumerated below :

(a) Alleged "guaranteed fadeless," for which only selected vat dyestuffs may be used.

(b) Fast to cotton bleaching, for which selected vat and azoic dyestuffs may be used.

(c) Fast to scouring, crabbing, stoving and cross-wool dyeing, for which selected vat, azoic, and sulphur dyestuffs may be used.

(d) Fast to light and washing, for which selected vat, azoic, sulphur, developed and direct dyestuffs may be used.

(e) Fast to washing, for which selected vat, azoic, sulphur, developed and direct dyestuffs may be used.

(f) Fast to light, for which selected vat, azoic, sulphur, developed and direct cotton dyestuffs may be used.

(g) Fast to perspiration, for which selected vat, azoic, sulphur, developed, basic (back tanned) and direct cotton dye-stuffs (in pale shades) may be used.

It may safely be said that the major quantity of rayon is still dyed with direct cotton dyestuffs, but the general trend in the textile trades for more reliable dyestuffs, coupled with the ever-widening range of fabrics in which rayon is being incorporated, is leading to a steadily growing demand for the fastest dyestuffs. This development is presenting the dyer with some very difficult problems, because the faster dyestuffs always require longer processing which is not conducive to the good condition of the rayon, particularly if dyed in the skein form.

One difficulty in the dyeing of continuous filament rayon which gives great trouble to the dyer is the liability to variation in the dyeing affinity of different skeins, which results in some skeins being lighter or darker than the major portion of the batch. This variation arising during manufacture has been shown to be due, in almost every case, to physical variations in the yarn, and cannot be detected until the yarn has been dyed. Variations can also occur on one and the same skein with equally undesirable results. It should be noted that such variations do not occur with staple fibre rayons, owing to the intimate mixing together of the fibres, providing widely different spinnings are not mixed. Although variations from skein to skein are very seldom due to chemical differences of the yarn, the variations on one and the same skein are occasionally due to over-bleaching. The distinction between chemical and physical variations is here emphasized, as in the following discussion any remarks relating to variable yarn are only applicable to yarns which show physical and not chemical variations. Experience has shown that some dyestuffs cover up any dyeing variations there may be in the yarn, whilst other dyestuffs show up any variation in a marked manner. It is, therefore, the business of the dyer to choose those dyestuffs which cover up this possible fault. This control in the hands of the dyer cannot be too strongly stressed.

It must not be overlooked, however, that uniform rayon can give uneven results if it is not correctly dyed, and it is necessary, therefore, to be able to decide whether the unevenness is due to faulty yarn or to faulty dyeing procedure. With most direct

cotton dyestuffs the method is simple ; the yarn is knitted, stripped with hot dilute caustic soda, and sodium hydrosulphite, and re-dyed. If the original unevenness repeats on re-dyeing the unevenness is due to faulty yarn. With mixings which contain yellows of the Oxyphenine type it is not possible to strip the dyeing to a white by using caustic soda and sodium hydrosulphite. This difficulty has been overcome as a result of an observation of Ratelade and Tchetvergoff (*Rev. Gen. des Mats. Col.*, Oct., 1928), who found that solutions of pyridine in water are capable of stripping direct dyeings to a white. Consequently dyeings with Oxyphenine as a component are stripped with a 25 per cent. solution of pyridine in water. Other substances which have also been found to strip this type of dyestuff and which are not as unpleasant to use as pyridine are ethyleneglycol monoethylene ether, cyclohexanone, etc. Such solutions, using caustic soda and sodium hydrosulphite in addition, will also strip most vat dyestuffs.

DIRECT COTTON DYESTUFFS

This class is the most suitable for the dyeing of rayons providing the fastness is sufficiently good for the particular article for which the rayon is intended. The duration of the dyeing process is the shortest of any class, it being quite possible to finish off simple shades in 20 minutes, whilst difficult compound shades may be matched off after 30 to 45 minutes in the dyebath itself. A large number of speciality products have been offered to rayon dyers which, it is claimed, if added to the dyebath favourably influence the levelling and winding of the rayon. Many of these products have been tried by the authors without being able to confirm the claims made, and none have been found in any way superior to a simple soap bath. The only use which has been found for these products is as an addition to the soap bath as a corrective for any hardness in the water. Such products are specialities of the type of the Gardinols, Igepons, Lissapols, and Calgon. The dyebath at 90° C. should be charged with the soap and the speciality product, and half the quantity of dyestuff. The dry yarn is then entered into the dyebath, and if dyeing on a machine a pattern may be taken in 10 minutes

from which it may be judged how much of the remaining dyestuff requires to be added to give the desired shade. Under normal conditions the dyer when using these dyestuffs is enabled to deliver the dyed material in the most favourable condition for subsequent processing, whilst they have no detrimental action on the handle of the rayon.

In the early days of viscose dyeing it was noticed that with the direct cotton dyestuffs the blues were usually more uneven dyeing than the yellows. (It must be understood that the term " even " is used throughout as meaning variation in shade between whole skeins, and not to patchiness on one and the same skein.) The first investigations on this subject were published by Wilson and Imison (*J.S.C.I.*, 1920, 39, 322T). Their paper included a list of dyes classified as " even " and " uneven " based on tests made on yarns of which the dyeing affinity had been deliberately varied. Subsequently the work of Wilson and Imison was developed so that several empirical methods for the classification of direct cotton dyestuffs with regard to the even dyeing of viscose rayon have been published. This work has shown that individual dyes vary considerably in their power to cover up the different dyeing affinities found in all commercial rayons.

The first empirical method (Whittaker, " Manchester Guardian Commercial," 1925, March 5, p. 31) was based on the observation that a relation existed between the even-dyeing properties of direct cotton dyestuffs and the extent of the capillary rise of their aqueous solutions on a viscose thread. By making this test under standard conditions it was found possible to attach to each direct cotton colour a so-called " suction number " which enabled its even-dyeing properties to be forecasted. Chrysophenine G (even dyeing) had a suction number 19, whilst Sky Blue FF (uneven dyeing) had a suction number 9.

In 1927 it was pointed out (Courtauld pamphlet " Dyeing of Viscose with Direct Cotton Dyestuffs ") that there are four properties possessed by those direct cotton dyestuffs which give the most even results on viscose rayon.

1. Those dyes which possess a high number as determined by the suction test give the most even results.
2. Even-dyeing dyes dye on at a rapid rate.
3. Viscose rayon dyed with even-dyeing dyestuffs when

boiled in a soap bath for $\frac{1}{2}$ hour along with an equal weight of undyed viscose rayon loses colour which dyes on the latter. The more closely the final shades of the dyed and originally undyed viscose rayons approximate to each other after boiling with soap the more suitable is the dye for viscose rayon.

4. Even-dyeing dyes require the least assistant in the dyebath.

The suction test was soon superseded by the temperature range test (1931 edition of above Courtauld pamphlet) since it enabled a sharper classification of direct cotton dyestuffs to be made.

This test is based on the observation that those dyes which show maximum affinity for viscose rayon at 20° C. give the most even results in large-scale work on commercial viscose rayon and those dyes which show maximum affinity at 90° C. give the most uneven results. The possible gradations of even-dyeing properties by this test are extremely sharp, because a dyestuff which has a maximum affinity at 30° C. is better than one possessing a maximum affinity at 50° C., the latter in turn being better than one possessing maximum affinity at 90° C.

Although the " temperature range " test shows that dyestuffs which possess the strongest affinity at the lowest temperature are the most even dyeing, it does not mean that they have to be dyed at this low temperature. The rule that viscose should be dyed at as high temperature as circumstances permit holds good. Those dyestuffs like Icyl Orange G, which dye viscose perfectly even at 90° C. give uneven results if dyed at 20° C.

The temperature range test proved to be extremely reliable until the introduction of faster to light, but unfortunately very uneven-dyeing, direct cotton dyestuffs. Large scale experience showed that those dyes which showed a maximum affinity at 90° C. exhibited wide variations in even-dyeing properties which could not be predicted by this test. Further work on the uneven-dyeing direct cotton dyestuffs culminated in a further empirical test (*Jour. Soc. Dyer and Col.*, 1932, p. 28), based on the fact that when equal weights of 150/21 and 150/36 viscose yarns were dyed together the latter always appeared fuller at the outset, but that if dyeing was continued long enough the former appeared fuller finally. All those dyestuffs which show maximum affinity

at 90° C. in the temperature range test may be differentiated by this further test. The shorter the time at which the 150/21 appears visually darker than the 150/36 the more even dyeing is that dye. Thus, Chlorantine Fast Blue GLL requires $1\frac{1}{2}$ hours at 90° C., whereas Chlorantine Fast Blue 3GLL requires 8 hours at 90° C. This classification agrees with large scale experience.

The 150/21 and 150/36 dyeing test has one very serious drawback, as the whole test depends upon a constant different in the dyeing and optical behaviour of the yarns, and as different batches of yarn vary greatly in dyeing properties different results would be expected from different yarns, thus making the test unreliable.

It is now generally agreed that the mechanism of direct dyeing is a process of diffusion in which an ultimate equilibrium between cellulose and dyebath is attained. It has also been shown that the production of an evenly dyed viscose depends upon the easy attainment of dyebath equilibrium, and that the rate at which direct dyes attain this equilibrium varies greatly from dyestuff to dyestuff. Those dyestuffs which attain the equilibrium in a normal dyeing time are " level " dyestuffs, whilst those which do not are " unlevel " dyestuffs.

A convenient method for measuring the time required for equilibrium to be attained is given in papers by Boulton and Reading (*J.S.D.C.,* 1934, p. 381 ; 1938, p. 268). Briefly the method is to determine colorimetrically the quantity of common salt required to give a 50 per cent. dyebath exhaustion when dyeing is allowed to proceed to equilibrium. By means of a series of time dyeings with this amount of common salt, the time required to give a 25 per cent. dyebath exhaustion is found. This is known as the " time of half-dyeing," and is found to give widely different figures for the direct dyestuffs which agree with works' experience. Thus Chlorazol Fast Orange G has a time of half-dyeing of 0·07 minutes, whereas Chlorazol Fast Orange AG has a time of half-dyeing of 155·5 minutes.

This test is therefore capable of drawing a much finer distinction between the direct cotton dyestuffs than any of the previously published empirical methods, and has the added advantage of giving results which are only dependent upon the uniformity of one yarn, whereas the 150/21 and 150/36 dyeing test depended upon a difference between two yarns remaining constant.

The following table shows the results obtained for a number of direct cotton dyestuffs by this method :

1. Chlorazol Fast Orange GS Icyl Orange GS	0·07
2. Icy Orange RS	0·10
3. Chlorazol Fast Helio 2RKS	0·18
4. Icyl Blue G	0·18
5. Rigan Blue 5R	0·21
6. Diazo Brill. Orange GR (C.I. 324)	0·22
7. Benzo Fast Yellow 4GL (C.I. 349)	0·26
8. Chrysophenine G (C.I. 365)	0·26
9. Diazo Sky Blue 3GL	0·29
10. Chlorazol Fast Black BKS	0·30
11. Chlorazol Yellow 8GS	0·33
12. Diazophenyl Red R	0·41
13. Chlorazol Violet RS (C.I. 388)	0·50
14. Rosanthrene Violet 5R	0·53
15. Triazogene Orange R	0·54
16. Diazo Brill. Scarlet B	0·74
17. Chlorazol Fast Red KS (C.I. 278)	0·84
18. Diazogene Red B..	0·88
19. Diphenyl Fast Red 7BL (C.I. 278)	0·88
20. Pyralon Orange G (C.I. 653)	0·88
21. Chlorazol Fast Bordeaux LKS	0·92
22. Diazo Geranine B	1·00
23. Rigan Sky Blue G	1·00
24. Primuline AS	1·00
25. Chlorazol Fast Yellow 5GKS (C.I. 346)	1·1
26. Rigan Blue R	1·1
27. Chlorazol Fast Helio BKS	1·2
28. Benzo Fast Helio 4BL (C.I. 353A)	1·2
29. Benzo Viscose Green BL	1·3
30. Benzanil Fast Brown 4GKS	1·3
31. Rosanthrene Pink (C.I. 324A)	1·4
32. Chlorazol Black SDS	1·5
33. Benzo Fast Yellow RL (C.I. 349A)	1·5
34. Benzo Fast Bordeaux 6BL	1·6
35. Chloramine Brill. Rose B	1·7
36. Brill. Dianil Blue 6G	1·8
37. Chloramine Fast Black B	1·8
38. Visco Black N	2·0
39. Diphenyl Fast Green 5GL	2·4
40. Viscose Blue Grey NB	2·5
41. Chlorantine Fast Bordeaux 2B	2·7
42. Diphenyl Brown F7	2·8
43. Rosanthrene Fast Orange R	2·8
44. Diphenyl Brill. Violet 3B	2·8
45. Chlorantine Fast Green 5GLL	2·9
46. Formaldehyde Navy Blue R	3·0
47. Sirius Supra Turquoise Blue G	3·0
48. Viscose Navy Blue NB	3·2
49. Brill. Benzo Green B	3·2
50. Diazo Brill. Orange 5G ex.	3·3
51. Viscose Copper Blue EG..	3·5
52. Diphenyl Fast Red B	3·5
53. Benzo Fast Light Scarlet 4BL	3·5
54. Rosanthrene Fast Bordeaux 2BL	3·5
55. Brill. Benzo Fast Yellow GL	3·8
56. Benzo Viscose Blue BF	4·0
57. Sirius Supra Blue FFRL	4·2
58. Sirius Red Violet RL	4·2
59. Diazamine Light Red N7B	4·4
60. Sirius Supra Blue GL	4·5
61. Chlorazol Dark Green PLS (C.I. 583)	4·5
62. Rosanthrene Fast Red 7BL	4·6
63. Sirius Supra Red 5B	4·8
64. Diphenyl Fast Brown DFH	4·9
65. Diazamine Light Bordeaux N2B	5·0
66. Benzo New Blue 5B	5·3
67. Diphenyl Fast Bordeaux B	6·1
68. Benzo Viscose Blue 3GFL	6·3
69. Diphenyl Fast Blue 3RL	7·6
70. Benzo Fast Orange 2RL..	7·6
71. Solar Red 2BL	8·0
72. Direct Brill. Pink 3B	8·4
73. Chlorazol Blue GS	8·4
74. Viscose Blue G	8·8
75. Solar Brill. Blue A	8·8
76. Benzopurpurine 4B (C.I. 448)	8·9
77. Rigan Blue G	8·9
78. Oxyphenine GG (C.I. 814)	9·6
79. Chlorazol Fast Eosine B (C.I. 353A)	10·0
80. Paramine Hosiery Brown RG	10·0
81. Diazol Lt. Grey N4B	10·5
82. Diphenyl Brown BBN ex.	10·8
83. Rigan Sky Blue 4G	11·53
84. Benzo Fast Brown 3GL ..	·12·4
85. Formaldehyde Navy Blue G..	12·9
86. Solar Rubinole B	13·2
87. Benzo Fast Copper Yellow GGL	13·2

88. Chlorantine Fast Brown
BRLL .. .. .. 13·2
89. Sirius Supra Blue BL .. 13·9
90. Solar Azurine L .. .. 13·9
91. Diazo Indigo Blue 3RL .. 14·2
92. Trisulphon Fast Brown BL 14·9
93. Rosanthrene BN .. .. 15·6
94. Formic Black MTG .. 15·9
95. Diphenyl Brill. Blue FF
(C.I. 318) .. .. 15·9
96. Chlorazol Dark Blue BS .. 16·7
97. Benzo Fast Copper Violet
BBL .. .. .. 17·0
98. Diphenyl Fast Grey B .. 17·05
99. Chlorazol Steel Blue 6BS 18·3
100. Benzo Fast Copper Brown
3GL .. .. .. 18·3
101. Diphenyl Blue M2B .. 18·3
102. Solophenyl Red Brown .. 18·3
103. Direct Brill. Pink B .. 19·0
104. Solar Brown PL .. .. 19·1
105. Melanthrerine BH (C.I.
401) .. .. .. 19·1
106. Direct Green 2G .. .. 20·0
107. Chlorantine Fast Blue
GLL .. .. .. 20·0
108. Chlorazol Brown MS (C.I.
420) .. .. .. 21·0
109. Benzo Fast Copper Yellow
RL •• .. .. 21·5
110. Solar Brown 2G .. .. 23·0
111. Chlorazol Fast Blue 2BNS 24·1
112. Diazo Navy Blue 4159 .. 24·1
113. Diazo Brown 3RW .. 24·1
114. Rigan Sky Blue 2G .. 24·7
115. Chlorantine Fast Red
5GLL .. .. .. 24·7
116. Trisulphon Brown B (C.I.
561) .. .. .. 25·2
117. Benzanil Fast Brown B .. 25·8
118. Benzo Fast Copper Blue
GL .. .. .. 26·4
119. Benzo Fast Blue 4GL .. 26·4
120. Benzo Copper Blue BB .. 26·5
121. Chlorazol Green GS (C.I.
594) .. .. .. 27·7

122. Benzopurpurine 10B (C.I.
495) .. .. .. 27·7
123. Sirius Supra Green GGL.. 29·0
124. Chlorazol Fast Scarlet GS 33·2
125. Diazo Brill. Green 3G .. 34·8
126. Chloramine Black EC .. 34·8
127. Diazo Fast Green GL .. 36·5
128. Diazo Fast Blue 6GW .. 36·5
129. Chlorazol Dark Brown
CRN .. .. .. 39·0
130. Benzo Viscose Grey 5B .. 39·0
131. Direct Fast Orange SE .. 40·8
132. Diazo Black OT (C.I. 371) 42·8
133. Chlorazol Fast Scarlet 8BS 43·8
134. Chlorazol Black GFS .. 43·8
135. Benzoform Yellow GL .. 44·7
136. Solar Orange RGL .. 48·1
137. Diazo Fast Green GFL .. 49·2
138. Benzanil Fast Scarlet BSN 50·3
139. Chlorantine Fast Green
BL .. .. .. 55·2
140. Benzo Fast Blue 8GL .. 60·5
141. Chlorantine Fast Rubine
RNLL .. .. .. 67·9
142. Trisulphon Blue FO .. 72·8
143. Benzo Fast Copper Red RL 83·5
144. Solar Yellow 2R .. .. 85·5
145. Chloramine Copper Blue
3G .. .. .. 89·5
146. Chlorazol Fast Grey 2BKS 91·6
147. Direct Fast Scarlet SE .. 100·0
148. Sirius Supra Olive GL .. 100·4
149. Sirius Supra Green BL .. 100·4
150. Benzoform Yellow RL .. 110·0
151. Chlorantine Fast Blue
3GLL .. .. .. 126·4
152. Solar Orange 4G .. .. 126·4
153. Chlorazol Fast Orange
AGS .. .. .. 155·5
154. Diphenyl Fast Blue Green
BL .. .. .. 159·2
155. Chlorantine Fast Scarlet
BNLL .. .. .. 260·0
156. Chlorazol Fast Pink BKS
(C.I. 353) .. .. 280·0

On referring to this list it will be found that Chrysophenine G has a time of half-dyeing of 0·26 mins. and Diphenyl Sky Blue FF has a time of half-dyeing of 15·9 mins ; it is common knowledge that Chrysophenine dyes evenly whilst Sky Blue FF dyes unevenly. Again, the even-dyeing dyestuff Chlorazol Fast Black BK has a time of half-dyeing of 0·30 mins., whilst the uneven-dyeing dyestuff Melanthrene BH has a time of half dyeing of 19·1 mins.

The greatest utility of this list, however, is in indicating which dyestuffs will give the best results in compound shades. Ex-

perience has shown that some dyestuffs with high times of half-dyeing will give tolerably even dyeings in self shades, but that when mixed with other dyestuffs in some compound shades they give uneven dyeings. The grading of the dyestuffs by this test enables the dyer to avoid such compound shades, provided other and better dyestuffs are available. The rule is to choose dyestuffs with as near the same time of half-dyeing as possible, and to avoid, as far as possible, mixing those dyestuffs whose times of half-dyeing are wide apart. This may best be illustrated by the following examples.

The following three dyestuffs will given an even dyeing :

Chlorazol Fast Orange GS	..	..	..	..	0·07
Diazo Brilliant Orange GR	..	..	.	..	0·22
Chlorazol Fast Black BK	..	..	..	..	0·30

because the times of half-dyeing are low and reasonably near to each other, whereas an uneven dyeing will result from the use of :

Chlorazol Fast Orange AGS	..	..	..	155·5
Diazo Brilliant Orange GR..	..	..	..	0·22
Chlorazol Fast Black BK ..	..	..	..	0·30

because Chlorazol Fast Orange AG has a much higher time of half-dyeing than the other two components of the mixture. In general it will be found advisable to mix two dyestuffs of high times of half-dyeing rather than a dyestuff with a high time of half-dyeing and one with a low time of half-dyeing in cases where two dyestuffs with low times of half-dyeing are not available. A mixing of high and low times of half-dyeing dyestuffs always gives skeins which contrast more strongly in shade than a mixing of two dyestuffs with high times of half-dyeing ; though in the latter case the skein may contrast strongly in depth of shade, the tone of the varying skeins will be similar. A dyeing of a dyestuff with a high time of half-dyeing always looks more or less hungry and bare, whilst a dyestuff with a low time of half-dyeing gives a much fuller-bodied and war er shade.

If it were possible to dye viscose rayon for a sufficiently long time, that is until equilibrium is obtained, the problem of dyeing variable viscoses would not exist. In bulk dyeing this is not possible with the existing methods and machinery, as the yarn would be damaged to such an extent as to make it useless for subsequent processing. The length of time which a dyer may

keep a yarn in the dyebath and still have a yarn which is windable varies with the type of yarn. As a general rule fine filament and low denier yarns must be dyed for as short a time as possible, whereas coarse denier yarns can be worked for a much longer, but not an excessive time. It will thus be seen that the dyer has frequently to make compromises, for or many occasions he would like to prolong the time of dyeing in order to obtain more even results, but only experience can decide when this course is permissible.

In the early days of viscose dyeing it was frequently stated that viscose could be dyed like cotton by entering into a cool dyebath and then raising the temperature. This method has proved to be totally unsuitable for dyeing viscose rayon, and experience has shown that the best results are obtained by dyeing at as high a temperature (90° C.) as possible, and maintaining the high temperature during the whole time of dyeing. If the temperature of dyeing is too low there is a tendency for uneven dyeings to be produced as levelling is considerably reduced at low temperatures.

It is natural that attempts should have been made in order to find whether any substances assist in obtaining more even dyeings on variable viscoses. In the Courtaulds pamphlets of 1927 it was stated that frequently more even dyeings can be obtained with many direct cotton blues and greens as self shades or in combination with direct cotton yellows if 2–5 per cent. Monopole oil and 1–2 per cent. formic or acetic acids are used as assistants instead of salt. Many other products have been proposed for this purpose, but the only product which has been found to be of any practical advantage is B-naphthol. The proposed method (B.P. 314,691) involves the use of 1 per cent. solution of B-naphthol+1 per cent. solution of common salt at 90° C., either as an addition to the dyebath or as an after-treatment to correct uneven dyeings. It has since been shown that the function of B-naphthol is to reduce the time required for equilibrium between yarn and dyestuff to be reached.

Viscose rayon, if not carefully dyed, can give uneven results which are in no way due to variations in the yarn. Methods for distinguishing between these faults and those due to faulty yarn have been described earlier (see p. 247).

It has already been stated that for the dyeing of compound shades the most successful results are obtained by using those dyestuffs possessing the same affinity or rate of dyeing on to the viscose. In certain cases, although dyestuffs possessing the same affinity have been used, uneven dyeing has resulted, and experience has shown that the cause of the uneven dyeing is due to the following causes :

(1) When viscose yarn is entered into a dyebath one end of the skein is naturally dyed before the other end, and the outside layer of threads dyed before the threads inside the skein. Consequently initially the dyeing is uneven. Owing to the fact that when using the Gerber type of machine the whole batch of yarn can be entered into the dyebath at once, and is actually turned over in one minute ; a more even result is obtained on this machine than is ever possible when the dyeing is done on a hand-box. With the even-dyeing dyestuffs of the Chlorazol Fast Orange G type initial unevenness is relatively unimportant as dyestuffs of this type level quickly. It is only with uneven-dyeing dyeings of the Chlorazol Fast Orange AG type that initial unevenness is definitely disadvantageous as these dyestuffs level very slowly. It follows, therefore, that any method which will open the skeins and so allow access of the liquor to the inside of the skeins will tend to give a more level result. To this end the yarn is opened whilst rotating on the machine by pulling the yarn over the rollers by hand in the direction in which the rollers are rotating. Practical experience has shown that opening of the yarn by this method is very successful and does not damage the yarn when done carefully by experienced dyers. Such hand-turning is, of course, necessary after each dyestuff or salt addition.

In the case of package dyeing with a large mass of rayon in a machine circulating a relatively small volume of liquor dyeing proceeds in a small liquor ratio, and poor penetration is frequently obtained. As the liquor moves through the package it is progressively exhausted and penetrates to the least accessible portions after having been exhausted by the more accessible portions. Poor penetration is found to be most marked in the case of dyestuffs which tend to become quickly exhausted in a small volume of liquor.

As the extent of the exhaustion is not generally appreciated,

the percentage exhaustion in 10 volumes after dyeing at 90° C. for 20 minutes without salt, of a number of direct cotton dyestuffs is given in the following table :

1% Benzo Fast Blue 4GL .. 41	1% Diazogene Red B 83
1% Benzo Fast Blue 8GL .. 18	1% Diazol Lt. Bordeaux N6B .. 41
1% Benzo Fast Light Scarlet 4BL.. 38	1% Diazol Lt. Grey N4B 32
1% Benzo Fast Orange 2RL .. 30	1% Diazol Lt. Yellow N4J .. 58
0·56% Benzopurpurine 4B 180%.. 91	1% Diphenyl Brilliant Violet 3B .. 51
1% Benzo Viscose Blue 3GFL .. 22	1% Diphenyl Fast Blue Green BL.. 20
1% Brilliant Benzo Fast Yellow GL 54	1% Diphenyl Blue M2B 60
1% Brilliant Fast Blue 3BX .. 22	0·33% Diphenyl Blue M2B 300% 19
1% Chloramine Brilliant Rose B .. 30	1% Diphenyl Fast Blue 3RL .. 34
1% Chloramine Brilliant Rose 3B.. 45	1% Diphenyl Chlorine Yellow FF 76
1% Chloramine Purple 10BC .. 88	0·33% Diphenyl Chlorine Yellow
1% Chlorantine Fast Blue GLL .. 59	FF 300% 57
0·5% Chlorantine Fast Blue GLL	1% Diphenyl Fast Red 7BL .. 64
200% 27	0·56% Diphenyl Fast Red 7BL
1% Chlorantine Fast Blue 3GLL.. 35	180% 33
1% Chlorantine Fast Brown BRLL 74	0·6% Diphenyl Sky Blue FF 165% 44
1% Chlorantine Fast Brown 8GLL 72	1% Direct Fast Black B 67
1% Chlorantine Fast Bordeaux 2B	1% Direct Fast Orange SE .. 66
conc. D 27	1% Direct Fast Scarlet SE .. 52
1% Chlorantine Fast Green BL .. 19	1% Direct Green 2G 66
1% Chlorantine Fast Green 5GLL.. 45	1% Durazol Fast Rubine BS .. 9
0·5% Chlorantine Fast Red 5GLL	1% Durazol Fast Violet 2BS .. 10
conc. D 10	0·56% Formic Black MTG 180%.. 72
1% Chlorantine Fast Rubine RNLL 19	1% Icyl Blue 2RS 80
1% Chlorantine Fast Violet 4BLN 51	1% Icyl Orange R 38
0·55% Chlorantine Fast Yellow	1% Icyl Orange GS 63
4GLL 182% 38	1% Melantherene BH 61
1% Chlorazol Brown MS 90	0·42% Paramine Black BH 240%.. 46
1% Chlorazol Dark Green PLS .. 78	1% Primuline 63
1% Chlorazol Fast Black BKS .. 74	0·625% Pyralon Orange G 160% .. 53
0·5% Chlorazol Fast Black BKS	1% Rigan Blue G 45
200% 46	1% Rigan Blue R 44
1% Chlorazol Fast Black SDS .. 77	1% Rigan Green G.. 25
1% Chlorazol Fast Blue 4GKS .. 43	1% Rigan Sky Blue G 53
1% Chlorazol Fast Bordeaux LKS 52	1% Rigan Sky Blue 4G 62
1% Chlorazol Fast Helio BKS .. 69	1% Sirius Brilliant Blue RL .. 16
1% Chlorazol Fast Helio 2RKS .. 59	1% Sirius Red Violet RL 13
1% Chlorazol Fast Orange·AGS .. 40	1% Sirius Supra Blue BL 10
1% Chlorazol Fast Orange GS .. 63	1% Sirius Supra Blue FFGGL .. 22
1% Chlorazol Fast Orange RKS .. 85	1% Sirius Supra Grey VGL .. 53
1% Chlorazol Fast Pink BKS .. 25	1% Sirius Supra Olive GL.. .. 38
1% Chlorazol Fast Red FGS .. 68	1% Sirius Supra Turquoise Blue G 9
1% Chlorazol Fast Scarlet 8BS .. 40	1% Solar Orange RGL 26
1% Chlorazol Fast Yellow 5GKS.. 74	1% Solar Rubinole B 27
1% Congo Orange R 62	1% Solar Yellow 2R 180% .. 45
1% Diazo Brilliant Orange GR .. 67	1% Solophenyl Red Brown .. 44
1% Diazo Geranine B 89	1% Triazogene Orange R 60
1% Diazo Indigo Blue 3RL .. 58	1% Viscose Blue Grey NB .. 54
1% Diazo Sky Blue 3GL 66	1% Viscose Navy Blue NB .. 61

By reference to the above list and remembering that dyestuffs having high times of half-dyeing dye slowly whereas dyestuffs having low times of half-dyeing dye rapidly, it is possible to choose suitable dyestuffs for package dyeing. For example, Chlorazol

Fast Orange AG which only exhausts 40 per cent. and has a time of half-dyeing of 155·5 minutes gives good penetration in package dyeing, whilst Benzopurpurine 4B 180 per cent. which exhausts 91 per cent. and has a time of half-dyeing of 8·9 minutes has poor penetrative properties. It must not be forgotten, however, that the depth of shade plays an important part in package dyeing, and that in general dark shades give better results than light shades.

Fabric selvedges and tightly twisted threads are in effect small " packages " of yarn, and the above considerations apply. In these cases, however, the dyed and undyed parts are in close proximity : with the even-dyeing dyestuffs levelling, by transference of dyestuff from one to the other, can readily take place which finally results in good penetration. But in package dyeing such close proximity of dyed and undyed parts does not occur generally throughout the package so that such levelling does not occur to the same extent, and a good result can with most dyestuffs only be obtained under conditions such as allow the dyestuff to be applied uniformly throughout the package from the outset.

(2) It is well known that the direct cotton dyestuffs vary considerably in their sensitivity towards common salt, but it is doubtful whether it has been realized previously how sensitive certain dyestuffs are to such additions. This sensitivity to salt is not of very great importance when dyeing on the Gerber machine with the even-dyeing direct cotton dyestuffs, but with the uneven-dyeing direct cotton dyestuffs the sensitivity of a dyestuff to salt is of vital importance. The following percentage exhaustion list shows the variations in the sensitivity of several direct cotton dyestuffs to common salt when dyed for 20 minutes at 90° C. in a liquor ratio of 40 : 1.

Dyestuff	Percentage salt				
	0	0·5	1	2	5
	%	%	%	%	%
1% Chlorazol F. Orange AG	1	9	10	16	31
1% Solar Rubinole B	7	11	13	15	26
1% Sirius Supra Grey VGL	11	16	27	36	56
1% Solar Yellow 2R 180%	16	20	24	30	49
0·5% Chlorantine F. Blue GLN 200%	15	17	20	30	56
1% Chlorantine F. Blue 3GLL	9	11	14	20	33
1% Solophenyl Red Brown	9	15	18	28	51

Dyestuff	Percentage salt				
	0	0·5	1	2	5
	%	%	%	%	%
1% Solar Orange RGL	5	8	12	19	38
1% Chlorazol F. Black BK..	25	30	33	40	54
1% Chlorazol F. Orange G	31	33	34	38	45
1% Diazo Brilliant Orange GR	32	33	35	38	45
0·63% Pyralon Orange G 160%	17	21	24	30	50
1% Chlorazol Fast Bordeaux LK	20	22	27	32	44

From these figures it is apparent that if a Chlorazol Fast Orange AG dyeing is being made, using 5 per cent. common salt as assistant, the salt must be gradually added to the dyebath. If the salt is added in one lot the outside threads of the skeins will be more heavily dyed than those in the middle of the skein as even small additions of salt exhaust quickly a relatively large proportion of the dyestuff. Since Chlorazol Fast Orange AG has poor levelling properties the resultant dyeing would be uneven.

These considerations apply to a still greater extent where low liquor ratios are used, as in package and jig dyeing, because under these conditions the direct cotton dyestuffs are still more sensitive to salt. This is shown by the following comparative exhaustion figures for 20-minute dyeings at 90° C.

1 PER CENT. CHLORAZOL FAST ORANGE

Common salt %	GS		AGS	
	10 vols. %	40 vols. %	10 vols. %	40 vols. %
0	63	31	40	1
0·5	69	33	47	9
1·0	75	34	54	10
2·0	81	38	69	16
5·0	83	45	83	31

0·75 PER CENT. CHLORANTINE FAST BLUE GLL 200 PER CENT.

Common salt %	10 vols. %	40 vols. %
0	12	3·0
0·5	38	5·0
1·0	58	8·0
2·0	82	18·0
5·0	96	44·0

From this table it will be seen that 1 per cent. salt in 10 volumes increases the exhaustion of Chlorantine Fast Blue GLL 200 per cent. by 46 per cent., which is equal to the exhaustion obtained with 5 per cent. salt in 40 volumes.

A test which gives valuable information on the best method of salting the uneven-dyeing dyestuffs is the following : Sufficient dye-liquor is prepared for eight 5-gram dyeings, divided equally into eight dyepots, and the temperature raised to 90° C. Eight viscose rayon skeins of 5 grams weight are then entered into the dye-liquors and dyeing continued for 10 minutes. One of the skeins is then taken out, and its dye-liquor neglected. To the other seven dye-liquors is added a portion of the salt, and dyeing continued for a further 10 minutes when a second skein is taken out, and its dye-liquor neglected. This process is continued until all the skeins have been removed from their dye-liquors, so that the last skein to be removed has been dyed in all for 80 minutes. The same liquor ratio is used as will be used on the large scale, and additions of water must be made to the dye-liquors during the dyeing to allow for evaporation. After drying, the skeins are examined, when it will readily be seen if any sudden increases in depth of shade occur after the salt additions. If such increases do occur the salt additions require to be adjusted until a gradual increase in depth is obtained. Practical experience has shown that with the uneven-dyeing dyestuffs the addition of the total amount of salt in one-sevenths gives good results when using 10 per cent. of salt, and in one-tenths when using more than 10 per cent. salt. This test is particularly valuable when dyeing compound shades, as it enables dyestuffs which are equal in salt sensitivity to be chosen for such shades.

(3) Unlevel dyeings can also be caused by the drainage of the dye-liquor to one end of the skein when the yarn is lifted from the dyebath after matching off. This is due to the fact that the small volume of liquor which is retained by the skein (about 3–5 times the weight of yarn) is, in the case of even-dyeing dyestuffs which have a good affinity cold, completely exhausted of its residual dyestuff, and as the liquor naturally runs to the lower end of the skein this end is dyed a slightly heavier depth than the other end. This defect can be overcome by using more salt during dyeing so that the direct cotton dyestuffs are more nearly dyed

to exhaustion and the residual dye-liquor has, therefore, very little dyestuff present in it.

At this stage, a fact which is not always fully appreciated might be stressed, viz. : that the filament denier size of a fibre controls the depth of shade of a dyeing ; the amount of dyestuff required to give any shade being greater on a fine filament denier than on a coarse filament denier yarn owing to the greater surface area of the fine filament denier yarn. Thus 150/72 viscose rayon requires more dyestuff than 150/27 viscose rayon to produce the same depth of shade because the ratio is 2 denier as against 5·5 denier per filament. This fact is frequently forgotten even by experienced people and has led to the statement that " Fibro " requires more dyestuff to obtain a given depth of shade than does continuous filament viscose.

Since the common filament deniers of cotton spun viscose staple are 1·25 and 1·5, it is, of course, no use expecting the same amount of dyestuff on these sizes of filament to give them the same depth of shade as on 150/27 viscose rayon with a filament denier of 5·5, whereas worsted spun staple fibre of 4·5 filament denier will give almost the same depth of shade as the 150/27 rayon. On the other hand, 1·25 and 1·5 filament denier viscose staple will give similar depths of shade with the same amount of dyestuff as American cotton (filament denier 1·69).

That the differences in depth shown by the various filament denier yarns is purely optical can be shown by the following example : Viscose staple of 4·5 filament denier and 1·5 filament denier were dyed with Chlorazol Fast Black BKS in separate dyebaths for ½ hour at 90° C. The exhaustion of the dyebaths after ½ hour was the same in each case, viz. : 64 per cent., yet the optical appearance of the yarns was quite distinct, the 4·5 filament denier yarn giving a much heavier shade than the 1·5 filament denier yarn.

These considerations also explain why equal depth dyeings of direct cotton dyestuffs on 1·5 filament denier viscose staple and cotton, have similar wet fastness properties, and why the fastness on these fibres is inferior to that on 5·5 denier continuous filament viscose rayon, as the amount of dyestuff required to give the same depth of shade on the continuous filament rayon is less than that required on 1·5 filament denier viscose staple or cotton.

Cuprammonium Rayon.—Of the regenerated cellulose rayons cuprammonium rayon has the greatest affinity for the direct cotton dyestuffs and nitrocellulose rayon the least, with viscose rayon occupying an intermediate position. For detailed information on the dyeing of this rayon the reader is referred to articles by Higgs (*J.S.D.C.*, 1936, p. 209 ; 1937, pp. 305, 461).

The Dyeing of Cellulose Acetate Rayons

Although a certain amount of cellulose acetate rayon is dyed in skein form, it is more usually dyed as knitted or woven fabric. The fact that cellulose acetate rayon has no affinity for direct cotton dyestuffs makes it possible for mixed fabrics of acetate rayon, regenerated cellulose rayons and cotton to be dyed solid or contrasting shades in one dyebath by use of acetate and direct cotton dyestuffs; this renders the yarn dyeing of acetate rayon largely unnecessary. Yarn dying is only necessary for a limited number of uses—*e.g.* yarns for cable wrapping and for yarns dyed in a fastness which is not possible with the usual acetate rayon dyestuffs. Like the regenerated cellulose rayons it loses appreciably in strength when wet, and therefore requires to be mechanically handled just as carefully as the latter, so that the remarks on the handling and manipulation of viscose rayon (p. 239) apply with equal force when dyeing this type of rayon.

It should also be noted that when dyeing skeins wooden dyebaths should be lined with Monel metal or stainless steel as with unlined dyebaths the wood becomes soft, wood fibres detach themselves, float in the dye-liquor, and become firmly attached to the threads. The dyebaths should also be of sufficient width and depth to prevent the yarn floating against the hot metal sides or bottom as this may cause dull patches on the skeins. For the same reason steam-pipes must be so placed that it is impossible for the yarn to come into contact with them, or alternatively the pipes should be of the loose type which can be lifted completely out of the dyebath after the dye-liquor has been heated to the required temperature.

With woven fabrics which are dyed on the jigger, it is advisable to sew on to the face of the piece end of the cotton wrapper coming into contact with the face of the fabric, a length of old

material made from 100 per cent. cellulose acetate rayon. If this is not done, the first few yards of the actual piece at either end are usually dyed a darker shade than the rest of the batch, as the cotton wrapper picks up the dyestuff without absorbing it, and this extra percentage of dyestuff is immediately absorbed by the first few yards of the piece in direct contact with it. Again, the wrappers and pieces should be sewn together with a suitable thread made from cellulose acetate rayon, as a cotton thread will mark off on to the pieces in the same way. It is also essential that woven pieces and knitted pieces should be received by the dyer as free from cracks and creases as is commercially possible, as if they are in a very cracked or creased condition they are liable to " crows' feet " due to the cracks and creases dyeing a heavier shade.

As cellulose acetate rayon when subjected to the action of water at too high a temperature loses its lustre, care must be taken that the use of dyebaths at temperatures above 80° C. are avoided if the lustre is to be retained. In many cases, however, a dull finish is desired, and dyeing may then be done at the boil.

The lack of affinity of cellulose acetate rayon for most dyestuffs which are used for cotton and regenerated cellulose rayons was a source of the gravest anxiety in the early days of its commercial production. This led to the trial by a number of workers of a large number of individual dyestuffs from various dyestuff groups, including the Basic, Gallocyanine and Azo groups, in an endeavour to satisfy this need. Sanderson (*J.S.D.C.*, 1922, p. 162) gives a list of such dyestuffs, many of which were marketed as the Cellutyl dyestuffs. From a practical point of view these were not fully satisfactory as the range was incomplete, and the fastness of several left much to be desired. Subsequent work on this subject proceeded on two lines. The first involved the saponification, or surface removal of acetyl groups, of the rayon by means of alkaline treatments which produced a film of cellulose having an affinity for dyestuffs normally used for dyeing cellulose, and the second was the production of dyestuffs and dyeing methods specifically for cellulose acetate rayon which did not involve saponification. Although historically the saponification methods are the older, such methods are now

only used in special cases, so that the development and application of the special dyestuffs for cellulose acetate rayon are described first.

The Ionamines, The "Dispersion Dyestuffs," and the Solacet Dyestuffs.—The first step forward in the development of special dyestuffs for cellulose acetate was made by Green and Saunders (*J.S.D.C.*, 1923, p. 10 ; 1924, p. 138) who introduced the Ionamines. The principle employed was the conversion of insoluble azo compounds containing amino groups by means of formaldehyde-bisulphite into methyl-ω-sulphonic acids which are water soluble. These gradually hydrolyze during the dyeing process, and the regenerated insoluble azo compounds are absorbed by the cellulose acetate rayon. They are dyed with the addition of 1–2 per cent. formic acid (Ionamine A with 1–2 per cent. soda ash). Since they contain a primary amino-group a variety of shades can be produced by diazotizing on the fibre and developing with B-naphthol, B-oxy-naphthoic acid, etc. This class of dyestuffs augmented the range of shades on cellulose acetate rayon considerably, and, in addition, the developed shades were of good fastness to washing. Since the dyeing process is long and presents considerable difficulties in matching to shade, and as more satisfactory dyestuffs have been produced, the Ionamines have lost their importance.

At the present time the most important type of special dyestuffs for cellulose acetate rayon is the " Dispersion " class, which includes such dyestuffs as the Duranol, Dispersol, S.R.A. Celliton, Cibacet, Setacyl, Artisil, Supracet, and Serisol dyestuffs. The first members of this group were introduced in 1924 as a result of the work of Baddiley, Shepherdson, and the British Dyestuffs Corporation (E.P. 211,270 of 1924) who produced the first Duranol dyestuffs, and of G. H. Ellis and The British Celanese Company (E.P. 219,349 of 1924) who produced the S.R.A. dyestuffs—so called because sulpho-ricinoleic acid is used as the dispersing agent. These dyestuffs are mainly amino-anthraquinone derivatives, basic azo compounds, and other basic substances, which can be brought into a finely divided condition by grinding with dispersing agents such as Turkey Red Oil, soap, etc. These were followed by similar products of other manufacturers, so that a wide range of shades was placed at the disposal of the cellulose acetate rayon

dyer. The problem which had caused so much anxiety was thereby solved in a satisfactory manner, and made possible the production of shades of good fastness to light, washing, and perspiration. It must, however, be realized that there still exists a wide gap when a range of shades of equal fastness to the vat dyestuffs is required. On the question of fastness reference may be made here to the permanent fading of certain dyeings during storage and display, or during making up into garments. The early work of Meister, Lucius and Brüning (*Färber Zeitung*, 1913, p. 93) on the subject of gas fading, as it is now called, describes the action of nitrous acid (produced from naked arc lamps) on dyed cotton and wool fabrics, and the explanation given is that the fading was probably due to the action of nitrous acid upon amino or substituted amino groups present in the dyestuff. Although Goodall (*J.S.D.C.*, 1930, p. 264) also quotes cases with other fibres, including pure silk stockings (see also Keyworth, *ibid.*, 1933, p. 245) most of the complaints of this type concern acetate rayon. As regards acetate rayon, this defect is caused by the action of nitrogen oxides, generated by fumes, generally tailors' gas irons, gas lighting, etc., on certain dyestuffs, mainly blue and violet amino-anthraquinone acetate dyestuffs (see Rowe and Chamberlain, *J.S.D.C.*, 1937, p. 268). A considerable amount of work has been done on this problem, and it has recently been claimed that an acetate blue, Eastone Blue 2B, fast to gas fumes, has been produced. It is also of interest to note that, in general, the same dyestuffs are faster to gas fume fading on nylon than they are on acetate rayon. For further information on this subject, the original papers referred to above should be consulted. (See also Goodall, *ibid.*, 1932, p. 118; 1935, p. 126; Jones, *ibid.*, 1936, p. 291).

The application of the " Dispersion " dyestuffs is relatively simple although practical difficulties arise, as they inevitably do with all processes, old and new. When dyeing cellulose acetate rayon in the skein form the following method has been proved to give the best winding yarn. The dyebath is made up with 0·25 per cent. to 0·5 per cent. solution of soap, whilst the dyestuff is pasted up with water and homogenized previously to adding to the dyebath. The dry unscoured yarn is entered into the dyebath at 65° C. the temperature raised to 80° C. in 15 minutes, and

dyeing continued for 30–60 minutes at this temperature. After dyeing the yarn should be oiled in an emulsion of oil, using a mineral oil for yarn required for electrical work, and a vegetable oil for yarn required for textile purposes. After drying the yarn should be allowed to condition, as when hot yarn is handled it becomes charged with static electricity, and the threads repel each other, thus making handling very difficult. All cellulose acetate pieces require to be desized and scoured before dyeing. The desizing baths usually consist of alkaline soaps to which has been added a solvent (xylol) which does not affect the rayon, whilst scouring is generally done with soap and ammonia (see p. 55). As soap and Turkey Red Oil have a retarding action on these dyestuffs, dyeing is carried out in a dyebath containing 0·1 per cent.–0·25 per cent. solution soap for pale and medium shades. For heavy shades dyeing is best done in plain soft water or with the addition of 0·25 per cent. solution of Monopol soap. For bright shades scouring and dyeing takes place at 60°–80° C. or for dull finishes at 60°–100° C. during $1\frac{1}{2}$ to 2 hours.

The properties of the individual "Dispersion" dyestuffs vary considerably, and for the most satisfactory results in compound shades it is again necessary to choose dyestuffs having similar dyeing properties. By making temperature range tests by the method described for viscose rayon (p. 250) considerable help will be obtained in making a suitable choice of dyestuffs for compound shades.

Further help is also given by the following test which is known as the "Half-skein levelling" test.

Six four-gram skeins are wound from the same commercial skein, and half immersed in a dyebath containing the dyestuff +0·25 per cent. solution of soap for 30 minutes at 80° C. the ratio of liquor to yarn being 40 : 1. The undyed half of the skeins are then scoured in a 0·25 per cent. solution soap for 30 minutes at 80° C. and the whole of the skeins well washed in cold water to remove all soap from the yarn. Five of the skeins are then treated separately in 40 times their weight of water for $\frac{1}{4}$, 1, 2, 3, and 4 hours at 80° C. The following examples show the extraordinary differences of the "Dispersion" dyestuffs when examined as described above, and so yield data for the correct choice of dyestuffs for compound shades.

Dyestuff			*Levelling*
2% Silatose Fast Yellow 5GL Paste ..	..	..	Good after ½ hour
1% Dispersol Fast Yellow 3G Paste ..	..	..	,, 1 hour
0·5% Cibacet Yellow GN Powder ..	..	..	,, 2 hours
1·5% Dispersol Fast Yellow A Paste ..	..	..	,, 3 hours
0·5% Celliton Fast Yellow 5G Powder	..	..	Good after 4 hours
3·0% Setacyl Direct Yellow 2R Powder	..	..	Poor after 4 hours
4·0% Duranol Orange G Paste ..	..	..	Good after 4 hours
1·5% Setacyl Direct Orange 2R Powder	..	..	Poor after 4 hours
2·5% Dispersol Fast Orange A Paste	..	..	Very poor after 4 hours
2·0% Dispersol Fast Orange BS Paste	..	. ..	,, ,, 4 hours
3·0% Duranol Red 2B Paste ..	..	..	Good after 3 hours
3·5% Duranol Scarlet 3B Paste ..	..	..	,, 4 hours
2·0% Setacyl Direct Pink 3B Powder	..	..	Fairly good after 4 hours
0·7% Celliton Fast Pink F3B Powder	..	..	,, ,, 4 hours
2·5% Celliton Red R Paste ..	..	..	Poor after 4 hours
4·0% Dispersol Fast Red A Paste ..	..	..	Very poor after 4 hours
1% Duranol Violet 2R Powder ..	..	..	Good after 2 hours
1% Cibacet Violet 2R Powder ..	..	..	,, 2 hours
2% Celliton Fast Violet B Powder ..	..	..	Fairly good after 4 hours
1% Cibacet Violet B Powder	..	..	Poor after 4 hours
2·5% Duranol Brilliant Blue CB Powder	..	..	Fairly good after 4 hours
0·6% Acetoquinone Blue NR Powder	..	..	Moderate after 4 hours
1·7% Celliton Fast Blue Green B Powder	..	..	,, 4 hours
2·0% Setacyl Direct Blue GS Powder	..	..	,, 4 hours
4·0% Duranol Blue G Paste ..	..	..	Very poor after 4 hours
1·5% Cibacet Blue 2R Double Paste ..	..	..	,, ,, 4 hours

Difficulty is often experienced in dyeing heavy shades, because there appears to be a point beyond which the fibre cannot absorb further dyestuff. This saturation point varies widely with the various dyestuffs, and those which dye heavy shades easily, or as the dyer terms it "build up," are the most sought after. Duranol Brilliant Blue G is an example of a dyestuff which does not build up, whereas Duranol Brilliant Blue CB does build up. The former owing to its superior fastness to light is mostly used in the paler shades, whilst the latter is given preference in the heavy shades.

Unlevel dyeings may be corrected by a treatment in a 0·5 per cent. solution soap at 80° C. ; the length of time of treatment depending upon the extent of the unlevelness and on the dyestuffs used. Too heavy dyeings may also be stripped sufficiently by the above treatment : should this prove ineffective the addition of 2 gms. per litre of activated charcoal in presence

of a protective colloid (glue) to the soap bath will be found to assist further stripping.

Owing to the relative insolubility of the " Dispersion " dyestuffs it has not been possible to use these dyestuffs for dyeing cellulose acetate rayon by package dyeing methods. In 1936, however, a new series of dyestuffs for cellulose acetate rayon known as the Solacet dyestuffs, were introduced by the I.C.I. They are applied to cellulose acetate rayon by dyeing at 60°–80° C. and salting on just as the direct cotton dyestuffs are salted on to cellulose.

The mechanism of the dyeing of the " Dispersion " class of acetate dyestuffs is stated to be one of solid solution. Thus Reinthaler-Rowe (" Artificial Silk," 1928, pp. 210, 211) quote the following work of Kartaschoff (*Helv. Chim. Acta*, 1925, p. 928 ; 1926, p. 152) who has shown " that in the dyeing of cellulose acetate silk with aminoanthraquinone derivatives, which are insoluble in water, the fibre acts simply as a solvent capable of extracting the colouring matter from the dyebath, important factors being temperature and the presence of water. Chemical reaction takes no part in the process, which consists in the attraction of electro-positive colour bases by the negatively charged fibre, followed by solution of the colouring matter in the fibre substance. Kartaschoff has illustrated this beautifully by photomicrographs in the case of a suspension of 1-amino-4-hydroxy-anthraquinone. Thirty seconds after immersing the fibre in the suspension, it is seen to be partially covered with solid colouring matter. Three minutes later the surface of the fibre is coated so thickly with solid colouring matter that the actual fibre can scarcely be seen. After a quarter of an hour at 60° C. the surface colour has largely disappeared, whilst after an hour at 60° C. the solid colouring matter has dissolved completely in the fibre, which is transparent and evenly stained."

Further evidence in favour of the solid solution theory of dyeing is the fact that when cellulose acetate rayon and solid dyestuff, *e.g.* aminoanthraquinone, are put into a dry test-tube and kept warm for a few days, the rayon will be evenly dyed. (See Lawrie, *J.S.D.C.*, 1932, p. 30.)

How far the Solacets, which are soluble in water, fit in with this theory has yet to be determined.

A comparatively new method for dyeing acetate rayon con-
sists of the application of certain acid dyestuffs from alcohol
solutions. In this method the dyestuffs are dissolved in hot
water, and denatured alcohol sufficient to give a 75 per cent.
solution by volume added ; if the alcohol is acid it is neutralized
with soda ash. The yarn is immersed in this dyebath for 5–10
minutes at 25° C., wrung out, dried in the air, and soaped twice
or 15 minutes with 5 per cent. soap at 65° C. Dyeings made by
this method are fast to light, hot soap and peroxide bleaching
(Rayon and Staple Fibre Handbook, 1939, p. 383).

Dyeings on Saponified Cellulose Acetate Rayon.—The
saponification process is now mainly of historical interest, with the
exception that it offers a method for applying vat, Indigosol and
Soledon dyestuffs to cellulose acetate rayon which are necessary
for the production of shades fast to boiling and degumming on
yarns for effect threads, and for the production of certain shades
on printing cloths with the direct dyestuffs which have to be
discharged.

Rowe (Reinthaler-Rowe, " Artificial Silks," 1928, p. 207)
attributes the first adoption of this process to Mork (F.P. 416,752
of 1910) and the number of patents which have been taken out is
the best evidence of the amount of work done in attempting to
overcome the difficulties involved in order to make this method
successful. The idea is to produce a uniform surface removal of
the acetyl groups by saponification with hot. alkaline solutions
which enable the rayon to be dyed with those classes of dyestuffs
normally used for cellulose. The alkali first suggested was
caustic soda, but subsequently more even results were obtained
by replacing the caustic soda by other alkaline salts with a
milder saponifying action, such as trisodium phosphate, sodium
carbonate, etc. Theoretically the idea is sound, but its practical
application presents many difficulties, because in addition to the
tendency to produce uneven results due to more rapid saponi-
fication in one place than another, saponification inevitably
reduces the weight of the cellulose acetate rayon, and causes a
serious reduction in the tenacity of the fibre, especially in the wet
condition.

The direct cotton dyestuffs, the Indigosols, and the Soledons,
are applied to saponified cellulose acetate rayon by the methods

normally used for dyeing cellulose fibres, without any further loss in strength. In the case of the vat dyestuffs, which are applied from an alkaline solution, further loss in weight and tenacity occurs, but this is reduced to a minimum by the use of milder alkalies than caustic soda, such as trisodium phosphate, sodium carbonate, etc. The use of these alkalies is only possible with those vat dyestuffs, mainly the I.K. dyestuffs, which are capable of being vatted with such mild alkalies.

It will be apparent from the above that the dyeing of vat dyestuffs on saponified cellulose acetate rayon is not very satisfactory, and it is not surprising that methods not involving saponification have been proposed.

For the application of vat and azoic dyestuffs to unsaponified acetate rayon, see pp. 184 and 215.

In the case of the Indigosols, the incorporation of these dyestuffs in the spinning solution has been patented (Dosne process), but this method is only commercially possible when there is a large demand for certain specific shades.

Section XIV.—THE DYEING OF THE NEWER SYNTHETIC FIBRES

Casein Fibre. (Lanital, Tiolan, etc.).—Casein fibre in its present state of development is only suitable for use in blends with other fibres (wool, cotton, or staple fibre), the processing and use of self yarns or fabrics being impracticable, as this fibre when placed in hot water loses strength and becomes plastic. Research has been directed towards eliminating this defect and with some measure of success ; it must be recognized, however, that the war has diminished casein fibre development and production.

Although casein fibre has an affinity for most classes of dyestuffs the dyeing of blends with wool for general textile purposes presents many difficulties. It is not surprising, therefore, to find the dyeing separately of these fibres prior to blending recommended in the literature, since this offers better solidity and fastness of such blends. Casein fibre may be dyed in the loose state, *i.e.* as cut lengths, or as carded sliver or combed slubbing in top form. In this connection Thomas (Chemistry and Industry, 1939, p. 710) reports that although in Italy it is dyed loose to some extent in a condition suitable for blending, the bulk of the material is dyed in the form of carded sliver in the Obermaier type of machine. In order to obtain dyeings sufficiently fast to milling, Neosols, Immedial Leuco and Tiolanital dyestuffs are frequently employed which require soda ash and sodium hydrosulphite for solution. A fair range of sulphur dyestuffs can, according to Bunbury (*J. Text. Inst.*, 1939, p. 175) be applied by the bicarbonate process, that is, by dissolving the dyestuff in the recommended amount of sodium sulphide and dyeing at 30° to 70° C. for 1–1½ hours in a dyebath containing an amount of sodium bicarbonate equal to 4/5ths of the weight of dyestuff.

Casein Fibre-Wool Blends.—Since casein fibre absorbs alkali very readily, the scouring of blends with wool under alkaline conditions should be avoided ; use should be made of scouring

agents, such as the sulphated fatty alcohols, which can be used under neutral or acid conditions. In both the preparation and dyeing of fabrics it is always advisable to run with minimum stretching and creasing, more particularly at high temperatures; yarns should be thoroughly cooled with cold water before squeezing, wringing, etc., to prevent felting. When fabrics have to be milled it is necessary to run with the minimum applied pressure, the time and temperature of treatment, and the alkalinity of the liquor being reduced in proportion to the amount of casein present in the fabric. Materials containing casein fibre should be dried at as low a temperature as possible, since if too high a temperature is employed the material loses pliability; steam pressing and decàtizing produce the same result, *i.e.* the material becomes " boardy."

With the acid dyestuffs casein fibre dyes much more readily than does wool, thus, at the boil it reaches its maximum exhaustion in about 5 minutes, whereas wool requires about 40–60 minutes. It dyes as readily and deeply cold as at the boil, whereas wool does not dye to an appreciable extent cold, and the depth of shade increases with the increase in temperature. When acid dyestuffs are dyed on wool-casein blends, the acid dyestuff dyes on the casein first and subsequently boils off the casein on to the wool. The casein acts as a dyestuff reservoir and releases the dyestuff gradually to dye the wool. This property promotes more even dyeing than when dyeing the same acid dyestuffs on wool, particularly with aggregated acid dyestuffs.

Conversely, acid dyestuffs on casein fibre are not as fast to wet processing : this is particularly so with the molecularly dispersed acid dyestuffs which on washing in a 0·5 per cent. solution soap at 40° C. may be completely stripped off the fibre. The aggregated acid dyestuffs are much more level dyeing on casein fibre than on wool ; in general their dyeing behaviour and wet fastness properties are similar to those of the molecularly dispersed acid dyestuffs on wool. With acid dyestuffs the chief difficulty in obtaining solid shades on casein fibre-wool blends is that the casein fibre absorbs the dyestuff more readily than the wool. The conditions giving the more solid results are those which favour dyeing of the wool, namely to enter the material into the dyebath at the maximum practicable temperature, and

to allow sufficient time, not less than 1 hour, for levelling. Further help is also obtained by controlling the acidity of the dyebath since an insufficiency of acid at the start of dyeing retards the dyeing of the casein fibre.

One of the most successful outlets for casein fibre in conjunction with wool is in the felt hat trade. The hat bodies, containing up to 25 per cent. casein fibre for ladies' felt hats or up to 14 per cent. for men's felt hats, may be dyed by normal methods at the boil in paddle machines with level dyeing fast to light acid dyestuffs, with the addition of Glauber's salt. It is interesting to note that during the felting and acid-planking most of the casein fibre forms a stratum inside the felt to give a sandwich or insert effect, there being mostly wool fibres on the surface layers.

Many chrome dyestuffs behave similarly to the molecularly dispersed acid dyestuffs in that they tend to boil off the casein fibre, thus making it difficult to obtain complete exhaustion of the dyebath. As aluminium salts in conjunction with formaldehyde are used for hardening casein fibre (see p. 32) and are not subsequently removed, this metal acts as a mordant for many chrome dyestuffs yielding shades different from the normal chrome dyestuffs shade. Since aluminium lakes are usually of inferior fastness to the corresponding chrome lakes on wool, a reduced fastness on casein fibre is to be expected. Consequently, some dyeings of the chrome dyestuffs are very loose to milling whereas others are fast. With some chrome dyestuffs, *e.g.* Eriochrome Red B (C.I. 652) applied by the afterchrome process, the dyestuff is almost destroyed due to the liberation of formaldehyde on boiling the casein fibre in dilute acid solution. In such cases, Grundy (*J.S.D.C.*, 1939, p. 348) recommends boiling the fibre prior to dyeing with 1 per cent. sodium bichromate and 3 per cent. acetic acid followed by washing, in order to obtain a dyeing having the normal shade. The light fastness on casein fibre of both acid and chrome dyestuffs is, in general, equal to that of the same dyestuffs on wool.

The dyeing of casein fibre at 80° C. has been recommended by Borghetty (American Dyes. Rep., 1936, p. 538) in order to preserve the material, which is very liable to be damaged when boiled. This does not hinder exhaustion of the dyestuff, and with

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the molecularly dispersed acid dyestuffs the fastness is not impaired, but with the aggregated acid dyestuffs the fastness to milling is not as good as when dyeing is done at the boil. The most serious drawback to the application of the chrome dyestuffs at 80° C. is that many dyestuffs do not combine with chromium at this temperature to produce the desired insoluble lake. With other chrome dyestuffs development is not complete and the resulting shades become altered in subsequent wet processing.

Wittwer (Textilber, 1938, p. 40), suggests that dyeings of the Neolan dyestuffs on casein fibre alone should be made at the boil with the usual amount of acid (8–10 per cent. sulphuric acid) in order to obtain full development of shade and fastness. Such a treatment, however, damages the fibre and unless the dyeing is well washed after dyeing, complete disintegration may take place on drying. Satisfactory exhaustion may be obtained by the use of small amounts of formic acid or even ammonium sulphate, but the dyeings, although showing little or no change on washing for 20 minutes at 40° C. in a 0·5 per cent. soap solution, are not as fast as those of the same dyestuff applied to wool by normal methods : the light fastness is equal to that on wool.

Casein Fibre-Viscose Staple Fibre Blends.—The use of casein fibre in blends with viscose staple fibre has opened up a new field in cloth construction since for the first time a protein fibre can be satisfactorily processed on cotton spinning machinery to give light weight cloths possessing some of the heat retaining properties of a wool cloth.

As both fibres in such blends have an affinity for direct cotton dyestuffs it is possible to produce either solid shades or tone-in-tone effects depending upon the particular dyestuff used and on the conditions of dyeing. Those dyestuffs which have low times of half-dyeing (see p. 252) tend to dye more solid at low temperatures ; as the temperature is raised the casein fibre becomes darker and the staple fibre lighter. Thus a ½ hour dyeing of 1·5 per cent. Chlorazol F. Black BK. dyed with 15 per cent. common salt in a liquor to material ratio of 40 to 1 dyes the casein fibre lighter than the staple fibre at 30° C., the two fibres almost solid at 50° C., whilst at 90° C. the casein fibre is very heavily dyed compared with the staple fibre. On the other hand, direct

cotton dyestuffs with a high time of half-dyeing leave the casein fibre almost white at low temperatures, whilst at 90° C. the casein fibre may be the more heavily dyed or the fibres may be dyed solid. When dyeing at high temperatures the quantity of common salt used does not directly affect the amount of dyestuff taken up by the casein fibre ; an increase in the amount of common salt does, however, increase the amount of dyestuff taken up by the staple fibre. Thus, with Chlorazol Fast Orange AG, dyed at 80° C. for ½ hour without the addition of salt, a full shade is obtained on the casein fibre but the staple fibre is almost undyed, but with 30 per cent. salt the staple fibre is the more heavily dyed. At high temperatures the longer the time of dyeing the more heavily is the casein fibre dyed. These statements may be generalized by stating that the conditions which give the maximum depth of shade on the staple fibre (*i.e.* addition of common salt, and dyeing at a high temperature) are favourable for the production of solid shades on casein fibre-staple fibre blends.

The properties of casein fibre are such that most dyestuffs under most dyeing conditions will stain this fibre. It is, however, possible to obtain the casein fibre in blends with staple fibre practically white by using selected direct cotton dyestuffs, and dyeing in presence of common salt in a dyeliquor containing soap or alkali. Thus, Paramine Black BH when dyed for ½ an hour at 80° C. in a dyeliquor containing 30 per cent. salt and 10 per cent. soap leaves the casein fibre substantially unstained. Good reserves of the staple fibre may be obtained by using dyestuffs and methods used for such a purpose with wool-cotton unions. Contrasting shade effects may be obtained by dyeing the blends in presence of salt and soap with direct cotton and neutral dyeing acid dyestuffs, using of the latter those which do not stain rayon staple under such conditions of dyeing.

"**Rayolanda**" **X**.—This fibre was first shown by Courtaulds Limited, in March, 1938 (see Whittaker, *J.S.D.C.*, 1938, p. 261), but was only produced on an experimental scale prior to June, 1941, when it became available in 4½ denier-matt, in 2-in. and 6-in. staple lengths.

" Rayolanda " X is not a substitute for any existing fibre ; it is an entirely new fibre possessing unique dyeing properties and a distinctive handle. Although it has a viscose basis it may be

dyed with all classes of dyestuffs used for animal or cellulosic fibres (dispersed acetate dyestuffs excepted). Its affinity for individual members·of these classes of dyestuffs differs in many instances from that of other fibres so that by an intelligent selection of dyestuffs and dyeing conditions many interesting colour effects may be obtained in suitable blendings .with wool, " Fibro," and other cellulosic fibres. These effects may be obtained in a most economical manner by single-bath dyeing in the piece or in fancy folded yarns, thus enabling grey stock to be carried which may be dyed into specific colourings as and when required.

. **"Rayolanda" X and Wool Mixtures.**—Before wool is dyed it has to undergo one or more of the following wet processes : setting or crabbing, scouring, milling, bleaching, chlorination, or a combination of these. These processes vary considerably from firm to firm, so that only a general indication of their effect on " Rayolanda " X is given below.

The usual process of setting wool yarn by boiling in water causes some reduction in the dyeing affinity of " Rayolanda " X, so that the process should be as mild as possible with regard to the length of time and temperature of treatment. An addition of 2 per cent. formic acid (on the weight of material) to the setting bath minimizes the loss of dyeing affinity. In the crabbing of pieces the cloth is not normally in contact with large volumes of boiling water for so long a time as in setting, so that the reduction in dyeing affinity will be correspondingly less.

The variations in scouring procedure are legion, but although all the possibilities ·have not been explored, it may be stated generally that " Rayolanda " X withstands scouring satisfactorily. The newer detergents, Lissapols, etc., have a less effect on the dyeing affinity than soap or soda ash, and should be used when circumstances permit. Heavy milling reduces the dyeing affinity ; with light milling the change is proportionately smaller.

" Rayolanda " X-wool mixtures may be bleached with peroxide to a white equal to that obtained on 100 per cent. wool. In bulk working, steeping overnight in the cold in 2 vols. hydrogen peroxide containing 5 cc. ammonia (0·880) and 5 grams sodium silicate per litre has given satisfactory results. Sulphur stoving is not so effective as the above for obtaining a good white on the

" Rayolanda " X. A combined permanganate and bisulphite bleach gives a good white, but reduces the affinity of " Rayolanda " X for dyestuffs.

As regards non-shrink processes, the normal wet chlorination process causes some reduction in affinity, but with the " Drisol," W.I.R.A., Negafel and Irvine Bank processes the affinity remains unchanged.

Though possessing an affinity for dyestuffs used for wool, " Rayolanda " X cannot be said to dye like wool. Whereas wool takes up dyestuffs usually at the higher temperatures only, " Rayolanda " X takes up dyestuffs readily at the lower temperatures. When the two fibres are dyed in a blend it is advisable to start dyeing at 30°–40° C. and to continue at this temperature until the " Rayolanda " X has absorbed most of the dyestuff. As the temperature of the dyebath is raised the dyestuff gradually migrates from the " Rayolanda " X to the wool. This migration is controlled not only by the temperature of dyeing but also by the acidity of the dyebath; the higher the acidity the more rapid is the migration rate. From these facts it will be evident that materials in which the " Rayolanda " X is too heavily dyed may be corrected by further boiling, or by the addition of more acid ; if too light in shade, by lowering the temperature of the dyebath (providing previous boiling at too high a temperature has not been prolonged so as to cause a reduction in affinity), and, if necessary, by adding suitable acid dyestuffs. Alternatively, the " Rayolanda" X may be filled up on the dolly with suitable acid or direct cotton dyestuffs.

Many combinations of dyestuffs commonly used for all-wool materials give unsatisfactory results on " Rayolanda " X-wool blends, since the prerequisites for level results are not only that the dyestuffs should dye on at equal rates but also migrate from the " Rayolanda " X to the wool at equal rate, so that before using such combinations for bulk lots preliminary trials should be carried out. Again, it must be realized that a dyestuff has not necessarily the same fastness on " Rayolanda " X as on wool. This is particularly the case with some acid dyestuffs which are satisfactory to light on wool, but fugitive on " Rayolanda " X. The number of variations is less with the chrome dyestuffs.

As " Rayolanda " X has a cellulosic basis, the use of formic

acid in place of sulphuric acid is recommended, thus eliminating the possibility of tendering in cases where the acid may not have been thoroughly removed by washing.

(a) *Level Dyeing or Molecularly Dispersed Acid Dyestuffs.*— These dyestuffs are suitable for " Rayolanda " X-wool blends owing to their ease of application and the attractive tone-in-tone effects which may be obtained ; solid shades may also be obtained with selected dyestuffs. A suitable combination to give a tone-in-tone effect is Acid Yellow T (C.I. 640), Lissamine Fast Red BS, Solway Blue BNS (C.I. 1054) ; a solid shade may also be obtained with this combination if the temperature of the dye-liquor is not raised above 90° C. and the dyeing is not unduly prolonged. The use of 2–4 per cent. formic acid is recommended to which Glauber's salt may be added to assist levelling and penetration. " Fibro," " Seraceta,"" Cotopa " or cotton effect threads may be satisfactorily reserved by this method of dyeing.

(b) *Fast to Milling or Aggregated Acid Dyestuffs.*—These dye-stuffs find their chief application on " Rayolanda " X-wool blends in the production of heavy solid shades of good wet fastness, in particular, for navy and blue shades on suitings and for bright shades fast to washing, perspiration and sea water required for knitted outerwear and bathing costumes.

The distribution of the dyestuff on the two fibres is again governed partly by the acidity and temperature of the dyebath. The weakly acid dye-liquor and the mild boil usually adopted for this group of dyestuffs is favourable for the production of a heavy shade on the " Rayolanda " X.

The Goodall method of dyeing (*J.S.D.C.*, 1938, p. 45) may also be used and the difficulty of levelling and penetration is not so acute as with 100 per cent. wool. As in wool dyeing, the use of a little bichrome is recommended when dyeing blues of the Coomassie Navy Blue type. This type of dyestuff is not so suitable for obtaining good reserves on effect threads.

(c) *Neolan Dyestuffs.*—These dyestuffs may be used on " Rayolanda " X-wool blends using 8–10 per cent. formic acid in place of the more usual sulphuric acid. With the whole range of Neolan dyestuffs (Blacks excepted) the " Rayolanda " X is dyed to a pale tint much more pleasing than the dead white obtained on other cellulosic fibres : blacks give a medium depth

of shade on the " Rayolanda " X. The dyeings are of good fastness to light and washing, perspiration and sea water, and cellulosic effect threads are not stained.

It has been found (Courtaulds Limited, Wilcock and Tattersfield, E.P. 537,964) that the distribution of Neolan dyestuffs between the wool and the " Rayolanda " X when dyed together may be so controlled that practically all the dyestuff is absorbed by the wool or by the " Rayolanda " X, according to the dyeing conditions employed. This wide control is exercised by the addition of small amounts of tannic acid to the dyebath. If no tannic acid is present the wool is dyed the heavier, whereas if 1 per cent. tannic acid is added to the dyebath the " Rayolanda " X is heavily dyed and the wool only slightly tinted.

(d) *Chrome Mordant Dyestuffs.*—The mordanting of " Rayolanda " X in the presence of wool is governed by the same factors as the dyeing of " Rayolanda " X and wool. Thus, relatively more chrome mordant will be taken up by " Rayolanda " X from a sweet chrome bath than from an acid or reduced chrome bath. This, of course, will influence the subsequent effect produced in dyeing. In general, it may be said that the method is more suitable for producing tone-in-tone than solid effects, since under the most advantageous conditions only a small amount of chrome mordant can be fixed on to the " Rayolanda " X.

(e) *Metachrome Dyestuffs.*—Chrome dyestuffs applied by the metachrome process may be used satisfactorily to give either tone-in-tone effects with the heavier shade on the wool, or can be used for the production of solid shades of excellent fastness. The effect is controlled by selection of dyestuffs and the time taken in raising the temperature to the boil.

The usual wool-dyeing procedure is followed, starting the dyeing at 40°–50° C. with the addition of 3–8 per cent. metachrome mordant or corresponding amounts of a mixture of two parts ammonium sulphate and one part of sodium or potassium chromate. After reaching the boil, dyeing should be continued for $1\frac{1}{4}$–$1\frac{1}{2}$ hours to obtain full development. If acid is necessary for complete exhaustion, it should be remembered that this will have a tendency to decrease the depth on the " Rayolanda " X. As in 100 per cent. wool dyeing, this method of dyeing is not

the best for preserving the purity of effect threads, but noticeable staining will only occur in heavy shades.

Brown shades may be obtained with Metachrome Brown B, Solochrome Brown EBS, Monochrome Olive Brown G, Eriochrome Brown R, and similar dyestuffs, shaded with the usual shading dyestuffs. Blues are best obtained on a Coomassie Navy Blue basis, as is the usual practice with wool, and mode shades with the popular combination of Chrome Fast Yellow G, Omega Chrome Red G, and Alizarine Blue Black B. (C.I. 1085).

(f) *Afterchrome Dyestuffs.*—Unlike the metachrome process, this method is suitable only for producing tone-in-tone effects, except with blacks. Eriochrome Black E is suitable for producing maximum contrast in tone between " Rayolanda " X and wool, and Eriochrome Black T or Solochrome Black AS types can be used to form a basis for a solid black. Commonly used mixings such as Eriochrome Yellow O, Omega Chrome Red G, and Alizarine Blue Black B are suitable for mode shades, whilst attractive browns may be obtained by using Eriochrome Brown R or Omega Chrome Brown DME, and greens with Alizarine Brilliant Green G. This method is most suitable for reserving effect threads. A few dyestuffs such as Monochrome Red B and Metachrome Brown B are unsuitable for application to " Rayolanda " X by this method.

(g) *Direct Cotton Dyestuffs.*—Of particular interest for blends of " Rayolanda " X and wool are the direct cotton dyestuffs which may be used to give attractive tone-in-tone, dyed and white, or solid effects. Since direct cotton dyestuffs are faster to wet processing on " Rayolanda " X than on " Fibro " or cotton, dyeings of good fastness to washing are more readily obtained. Owing to the high affinity of the " Rayolanda " X for these dyestuffs, dyeing should be commenced at a low temperature (40° C.) and continued 10–20 minutes before raising slowly to the required maximum temperature. If a neutral dyeing acid dyestuff of contrasting tone is also added to the dyebath a two-tone effect may be obtained. It is easier to reserve the wool than is the case when " Fibro " or cotton are used because of this greater affinity, and higher temperatures may be employed in the dyebath without the use of auxiliaries of the " Taninol " type. Solid effects may be obtained by dyeing at the boil with

dyestuffs suitable for the union-dyeing method for wool and "Fibro," or cotton.

"Rayolanda" X and "Fibro" Mixtures.—All the classes of dyestuffs used for "Fibro" may be used for "Rayolanda" X. The latter fibre has, for the most part, a greater affinity for these dyestuffs than has "Fibro." It follows, therefore, that "Rayolanda" X/"Fibro" blends may be dyed with direct cotton, sulphur, vat, Soledon and azoic dyestuffs; in addition to which the "Rayolanda" X may also be dyed with dyestuffs used for wool.

It must be understood that yarn or fabrics consisting of "Rayolanda" X and "Fibro" do not require a kier boiling, but that a light scour will be sufficient. Since the dyeing affinity of "Rayolanda" X is reduced by severe scouring at high temperatures the scour should be carried out at as low a temperature as will give the required result, whilst full use should be made of the newer detergents. On no account must "Rayolanda" X be submitted to a normal hypochlorite bleaching process because such a process destroys the special affinity of "Rayolanda" X for dyestuffs. It may be bleached with peroxide without detriment.

Direct Cotton Dyestuffs.—This class of dyestuffs is capable of giving tone-in-tone or solid effects by control of the temperature of the dyeliquor and the amount of common salt used.

It has to be understood that the direct cotton dyestuffs have to be carefully selected to give the desired effects. For compound shades the golden rule of choosing dyestuffs which dye on at the same rate must be observed.

Tone-in-tone effects may be produced with the direct cotton dyestuffs by working at high temperatures and making only small or even no salt additions; the lower the amount of salt and the higher the temperature, the greater the contrast obtained with all direct cotton dyestuffs—the heavier shade being on the "Rayolanda" X.

By employing mixtures of neutral dyeing acid and direct cotton dyestuffs two-tone effects may be obtained. The neutral-dyeing acid dyestuffs will dye a heavier shade on the "Rayolanda" X than on the "Fibro," and by varying the conditions of temperature and salt addition the take-up of the direct cotton

dyestuff on the " Rayolanda " X and " Fibro " may be controlled.

It will be apparent that colour and white effects can be obtained by using dyestuffs which have no affinity for the " Fibro," but an affinity for " Rayolanda " X, viz. wool dyestuffs. The level dyeing acid dyestuffs may be used where no particular fastness is required, the optimum conditions being in the presence of 2 per cent. formic acid and at a temperature of 60°–90° C. To obtain greater wet fastness, the aggregated acid dyestuffs or certain chrome dyestuffs may be used, but greater difficulty will be experienced in preventing staining of the " Fibro."

Many of the most satisfactory direct cotton dyestuffs for producing solid shades on " Rayolanda " X–" Fibro " blends are those which dye slowly, such as Chlorazol Fast Orange AG. These dyestuffs may be found at the lower end of the list of dyestuffs given by Boulton and Reading (p. 252). It will be found that, in general, a more solid effect is obtained by increasing the amount of salt added, since the depth on the " Fibro " increases with increasing amounts of salt, whereas the shade on the " Rayolanda " X is less dependent on salt addition. Again, by lowering the temperature of dyeing, the more solid the effect, since the affinity of " Rayolanda " X is reduced relatively more by lowering the temperature than is that of " Fibro " ; it should be understood that with the direct cotton dyestuffs the tendency is for " Rayolanda " X to be dyed a heavier shade than " Fibro." Since the depth of shade on " Fibro " increases with decreasing liquor volume, whereas the affinity of " Rayolanda " X is relatively independent of liquor volume, it follows that the smaller the volume the more readily is a solid shade obtained. Although the dyestuffs which dye on slowly are the most satisfactory, by varying the dyeing conditions sufficiently on the lines indicated it is possible with many of the more rapid-dyeing dyestuffs to obtain solid effects.

Many of the direct cotton dyestuffs show a distinct improvement in washing fastness when dyed on " Rayolanda " X than when dyed on " Fibro " or other cellulosic materials, an advantage which enables the dyer in some cases to use dyestuffs for washing shades which normally could only be obtained either by suitable after-treatment or in some cases by the use of faster and more

expensive dyestuffs. On the other hand, the light fastness of many of the direct cotton dyestuffs is adversely affected, but a sufficient number are available to produce the wide variety of shades demanded in practice.

Sulphur Dyestuffs.—A number of sulphur dyestuffs can be used for the production of solid shades on " Rayolanda " X and " Fibro " in cases where a greater degree of fastness to washing is required than is obtained with the direct cotton dyestuffs. In medium and heavy dyeings, solid shades are obtained at 90° C., with the addition of 20 per cent. salt to the dyebath ; *e.g.* Thionol Black B, Pyrogene Direct Blue RL, and Pyrogene Brown 6R give solid shades. With light shades the " Rayolanda " has a greater affinity than " Fibro " which in some cases is left almost white.

Tone-in-tone effects may be obtained with these dyestuffs by working at low temperatures, *e.g.* 40° C., at which temperature a heavier shade is obtained on the " Fibro."

Vat Dyestuffs.—The vat dyestuffs may be used to produce either tone-in-tone or solid shades. When dyed with the usually recommended quantities of caustic soda and sodium hydrosulphite the " Fibro " is dyed heavier than the " Rayolanda " X at low temperatures, but, depending on the actual dyestuff used, the " Rayolanda " X dyes to the same depth or a slightly heavier shade as the temperature is raised,

Soledon Dyestuffs.—These dyestuffs give tone-in-tone effects on " Rayolanda " X and " Fibro " materials, the greatest contrasts being obtained with those dyestuffs possessing a low affinity for " Fibro," *i.e.* those requiring large amounts of salt to give maximum depth of shade when dyed on 100 per cent. " Fibro " (p. 219). For example, Soledon Blue RCS gives, in general, a greater contrast between the two fibres than is obtained with Soledon Jade Green. The degree of contrast is also influenced by the temperature of dyeing and by the amount of salt used, the higher the temperature of dyeing and the lower the amount of salt used the greater being the contrast between the two fibres. It is also to be noted that the development of shade of these dyestuffs on " Rayolanda " X is rather slower than on " Fibro."

It will be realized that the general principle underlying the dyeing of " Rayolanda " X and " Fibro " blends with direct

cotton, sulphur, vat and soledon dyestuffs is that the higher th temperature of the dyeliquor employed and the smaller th amount of salt that is present the heavier the shade produce on the " Rayolanda " X relative to the " Fibro."

When using vat dyestuffs common salt will only be added t those dyestuffs for which it is recommended if they are bein dyed on cotton.

Detailed lists of suitable dyestuffs have been published i Courtaulds' pamphlet on " Rayolanda " X, whilst the dyestui manufacturers have issued detailed information concerning thei own dyestuffs.

Nylon.—Up to the present time nylon has found its mai outlet as a textile fibre in the manufacture of hosiery, the hos being dyed with acetate rayon dyestuffs, after preboarding (see p. 34) and scouring in a liquor containing 1 cc. ammonia (0·880) and 3 gms. soap per litre at 60° C. for 20 minutes. A; development proceeds it is probable that the use of other classe of dyestuffs will be found necessary to give the desired fastness or effects when it is used alone or in combination with other fibres. Papers dealing generally with the dyeing of nylon have been published by White (*J.S.D.C.*, 1939, p. 409), Stott (Amer. Dyes. Rep., 1939, p. 582 ; 1940, p. 646), and Whattam (Textile Manuf., August, 1940), from which it may be stated that, as a general basis of comparison with other fibres, nylon dyes similarly to wool and silk with the important addition that it also has an excellent affinity for the acetate rayon dyestuffs.

Acetate Dyestuffs.—These dyestuffs may be applied to nylon by dyeing at 85°–90° C. for one hour in a dyebath containing soap or an auxiliary product such as the sulphated fatty alcohols.   In light or medium shades the depth of shade is not appreciably influenced by reasonable variations in the liquor ratio or by variations in the pH of the dyebath between pH7 and 10. Although all members of this class of dyestuffs dye nylon satis-factorily some differ in their affinity and shade from the recognized dyeings on acetate rayon.   White (*J.S.D.C.*, 1939, p. 411) gives a list showing the differences with a selection of Duranol and Dispersol dyestuffs (I.C.I.) ; a similar list of Du Pont acetate dyestuffs is also given by Stott (Amer. Dyes. Reporter, 1939, p. 589).   As a group these dyestuffs " build " up into dark shades

better than the acid and chrome dyestuffs. The washing fastness is slightly inferior to similar shades on acetate rayon, whilst the light fastness is similar with medium shades but somewhat less fast in pale shades. As the acetate dyestuffs on nylon have good levelling properties there is little danger of unlevel dyeings being produced and any " barriness " is effectively covered. Advantage may also be taken of their ease of levelling in converting left-over stock into usable shades. Thus, Whattam states that hosiery of different shades may be converted into a usable shade in one hour by treatment at 85°–90° C. in a bath containing 2 lb. of a synthetic detergent, 1 lb. soap, 0·5 lb. trisodium phosphate per 100 gallons. In the case of acetate diazo blacks, it is important that the developing bath should be at least of 0·1 grm. base per litre strength. The diazotization of these dyestuffs on nylon requires more sodium nitrite and hydrochloric acid than is necessary on acetate rayon, 7 per cent. sodium nitrite and 14 per cent. hydrochloric acid being a suitable quantity, the diazotization being carried out for one hour.

The water-soluble Solacet dyestuffs (I.C.I.) also have an excellent affinity for nylon, giving shades which are not quite as fast to washing as on acetate rayon, and which in some cases exhibit a notable difference in shade. Except in very heavy shades, the Solacet dyestuffs cannot be used for solid shades on nylon and acetate rayon, owing to the much greater affinity for the former fibre, but give solid shades on nylon-silk mixtures, as the affinity of the two fibres is about equal.

Acid Wool Dyestuffs.—Nylon may be dyed with most of the acid dyestuffs ; in light and medium shades the milling dyestuffs exhaust well from neutral or acid dyebaths, whilst the level dyeing dyestuffs require to be dyed in presence of sulphuric or formic acid. Compared with the dispersed acetate rayon dyestuffs they do not " build up " as well, are more sensitive to variations in dyeing conditions, nor are they as effective in covering " barriness " and other imperfections common to knitted materials. In dyeing mixtures of acid dyestuffs on nylon care is required in selecting those which dye at the same rate. In this connection White states that " In general the level dyeing dyes give satisfactory results, but Coomassie and Carbolan dyes exhibit unexpected differences in dyeing properties when present

in mixtures." Again, the neutral dyeing acid dyestuffs do not show the property of migration exhibited by the dispersed acetate dyestuffs, and so give dyeings of better fastness to washing than the latter. In all except pale shades their fastness to light on nylon is equal to that on wool.

Chrome Dyestuffs.—The general opinion appears to be that the chrome dyestuffs, with the exception of blacks, are not likely to be of very wide application on nylon, since by the chrome mordant and metachrome processes little development of the dyestuff takes place, whilst by the afterchrome process larger than normal amounts of acid and bichrome and frequently longer time of dyeing are required to produce satisfactory dyeings. Chrome Blacks, *e.g.* Solochrome Black WDFA, on nylon, give dyeings of excellent fastness to light and are superior in washing fastness to the acetate diazo blacks, but show inferior level dyeing properties.

Direct Cotton Dyestuffs.—The number of direct cotton dye-stuffs suitable for nylon when applied from a neutral dyebath is very limited, the affinity varying from almost zero, *e.g.* Chlorazol Sky Blue FF to a high affinity, *e.g.* Paramine Fast Red F. In some cases the affinity of these dyestuffs can be improved by the addition of 2–3 per cent. acetic acid to the dyebath. Direct cotton dyestuffs on nylon are faster to washing than, and of similar light fastness, to the same depth of shade on cotton or viscose rayon. In the case of the diazotized and developed direct cotton dyestuffs there is considerable difficulty in pro-ducing the fully developed shade. In all probability the direct cotton dyestuffs will find no great use for dyeing 100 per cent. nylon, although those dyestuffs normally used for dyeing cotton and leaving wool slightly stained may be used in dyeing nylon mixtures with cotton or viscose rayon to give the latter fibres the same shade as the nylon, *e.g.* cotton tops and feet for hose.

Vat and Soledon Dyestuffs.—The affinity of the vat dyestuffs when applied by normal methods varies widely. In general, the Indigoid type gives better colour value than the Anthraquinone type, as is the case with pure silk. According to the I.C.I. B.P. 530,485, better value is obtained with the Anthraquinone dyestuffs by vatting with caustic soda and a formaldehyde sulphoxylate or a formaldehyde hydrosulphite compound and

dyeing at 90°–95° C. The vat dyestuffs can also be successfully dyed on nylon by the method described for the application of these dyestuffs to cellulose acetate rayon (see p. 215).

Like the vat dyestuffs, the Soledon dyestuffs also show wide variations in their affinity for nylon, but this affinity may, in certain cases, be improved by the careful addition of acid to the dyebath. These dyestuffs give shades having excellent washing fastness, but the light fastness of many vat dyestuffs is inferior to that of the same dyestuffs on viscose rayon or cotton.

Other Dyestuffs.—Basic dyestuffs have a good affinity for nylon, but when dyed in the presence of silk the nylon is only stained. Their washing fastness is good, but as the light fastness is poor it is unlikely that they will find any other than specialized applications. As the sulphur dyestuffs generally have a very low affinity for nylon it is probable that these dyestuffs will be of no interest on this fibre.

When dyed by normal methods the Naphtol dyestuffs have little affinity for nylon. Their affinity can, however, be increased by dyeing in a solution containing a base, Naphtol, and sodium nitrite mixed together, followed by development in acid (see also p. 184). Better control of this method can be achieved by converting the free caustic soda into sodium carbonate by the addition of the requisite amount of sodium bicarbonate rather than by the addition of acetic acid to neutralize the caustic alkalinity (see also p. 215).

Section XV.—THE DYEING OF MIXED FIBRES, · INCLUDING GARMENTS

The dyeing of mixed yarns and fabrics is a branch of dyeing which is continuously increasing both in scope and importance. This development may be attributed mainly to two causes :

1. The increasing adoption of synthetic fibres, *e.g.* regenerated and basified cellulose and cellulose acetate rayons, for the construction of fabrics which has enabled designers to obtain novel effects hitherto unobtainable at a reasonable price.

2. The constant introduction of new coal-tar dyestuffs and products with special properties for use with mixed fabrics, which make it possible for the dyer to obtain satisfactory dyeings on these fabrics more readily.

The principal fibres available to the manufacturer are wool, cotton, mercerized cotton, silk, hemp, linen, jute, as well as both bright and delustred regenerated cellulose and cellulose acetate rayons, so that the possibilities in regard to mixed fibres is extremely large, particularly as sometimes more than two of these fibres are present in some fabrics. The production of casein fibre, " Rayolanda," and nylon on the commercial scale will inevitably lead to a still greater variety of mixed fibres as the special properties of these newer fibres are fully developed under normal conditions (see Section XIV.). There are numerous ways of making and dyeing such fabrics, the three main methods being :

1. The two or more fibres may be dyed separately and then woven to give shot or other effects, or the fibres may be dyed in the loose, scribbled together, then spun into yarn and woven, which is the method employed for cheap tweeds, etc.

2. One fibre, *e.g.* the cotton warp, may be dyed in the warp, hank, cop, or beam, then woven up with an undyed weft, which is subsequently dyed in the piece.

3. All the fibres may be woven in the grey state and subsequently dyed, not only in solid shades but also in multi-colours in the piece.

With such fabrics it is the general rule to dye the inferior fibre to a darker shade than the other fibres which are present.

In general, faster shades may be obtained by methods (1) and (2) than by method (3), but the latter method, in addition to being cheaper than the other methods, is preferable from the merchant's point of view, as it enables him to hold stock in the grey state which may subsequently be dyed at short notice to any desired shade.

Modern union dyeing, as now practised, may be said to have been made possible by the introduction of the direct cotton dyestuffs which enabled fabrics of silk, wool, cotton, and rayon, except the acetate variety, to be dyed a uniform shade in one bath. Before their introduction the dyeing of mixed fabrics was a long and complicated process, involving the use of many baths, demanding great skill and experience on the part of the dyer. Single-bath union dyeing involves careful attention to the temperature of the dyebath in order to regulate the dyeing of the various fibres to the same depth of shade, but the process is very quick and comparatively cheap. It must not, however, be assumed that the single-bath method is without drawbacks, because it has several disadvantages. The range of shades which may be obtained by this method is a limited though gradually increasing one—bright pinks, greens, and violets are still unobtainable by this method. Many classes of fabrics containing wool such as lustre goods, cannot be dyed by this method, which is frequently termed "soft dyeing" as compared with dyeing in an acid bath, for two reasons, viz. :

1. The lustre and handle of the goods is more depreciated than they are when dyed in an acid dyebath. Speakman and Cole (*J.S.D.C.*, 1938, p. 563) have shown that the harmful effect of "neutral" dyeing on wool is due to the fact that the pH of the dyebath, with soap scoured wool, is much higher than the optimum pH of 5·5, the pH at which attack on the disulphide bond is at a minimum. It is suggested that the remedy for the defect is to scour with a neutral detergent instead of soap, or to

use ammonium acetate in conjunction with sodium sulphate to eliminate excessive alkalinity of soap scoured wool or wool unions.

2. The goods are more liable to cockle and crease, whilst the dyestuffs used are not sufficiently fast to permit of subsequent crabbing in order to straighten the dyed goods.

Notwithstanding these drawbacks the single-bath method has become of great importance in modern dyeing practice.

The various methods of dyeing the chief classes of union or mixed goods will now be considered in more detail.

Wool and Silk Unions.—The majority of wool and silk unions appear on the market as light-weight·fabrics for ladies' wear. Such fabrics may be dyed either in solid shades or to give two-colour (shot) effects, whilst hosiery which consists of silk panels and wool toes and feet is dyed in solid shades, whereas wool hose with silk effect threads is usually dyed in two colours for the production of marl effects.

The silk must be degummed before commencing dyeing, but the degumming process commonly used for all-silk goods cannot be employed for wool and silk unions without felting the wool. By degumming at 80° C. the condition of the wool is not seriously endangered, but the process is not very satisfactory.

Two-colour effects are usually produced by a two-bath dyeing method. The material is first dyed with acid dyestuffs which dye the wool, but leave the silk white or nearly so at the boil. The method of procedure is to enter the material into the boiling dyebath containing Glauber's salt and acetic acid, and to continue the dyeing for $1-1\frac{1}{2}$ hours at the boil until the wool is on shade. The bath must be strongly acid, so that it is advisable to add acetic acid to the dyebath from time to time to replace that lost by evaporation. The dyestuffs in the list below leave the silk white or nearly so in a boiling acid dyebath :

Naphtol Yellow (C.I. 10)   Tartrazine (C.I. 640)
Xylene Yellows   Acid Magenta (C.I. 692)
Kiton Red S. (C.I. 54)   Indigo Extract (C.I. 1180)
Solway Blue B. (C.I. 1054)   Naphthylamine Black EFF (C.I. 246)
Orange 2G. (C.I. 27)

Staining of the silk in heavy shades can hardly be avoided, so that if the silk has to be left white or dyed a delicate tint, the silk must be cleared by one of the following methods :

(a) By working in a bath of clean soft water at 40°–60° C., alone or with the addition of a little ammonium acetate. This treatment always removes some dyestuff from the wool, so that it must be carried out quickly and with as small an amount of ammonium acetate as will clear the silk sufficiently to admit of the desired shade being obtained. When dyeing the wool, allowance must be made for this loss of depth of shade during the clearing of the silk.

(b) By working in a cold to lukewarm bath containing a little hydrosulphite. This treatment also removes some of the dyestuff from the wool.

(c) Another method is to run the pieces in a bath of aired water containing bran about $1\frac{1}{2}$ oz. to the gallon ; then wash well in cold water.

It is claimed that with selected dyestuffs the addition of 5–10 per cent. Setamol WS to the dyebath after dyeing for 1 hour at the boil, and then boiling for a further $\frac{1}{2}$ hour, renders subsequent clearing unnecessary.

After dyeing the wool, the silk is usually dyed from a cold dyebath containing acetic acid with selected basic or acid dyestuffs, but on no account may these two classes of dyestuffs be mixed. The silk may also be filled up at low temperatures with selected direct cotton dyestuffs : their affinity for silk at low temperatures is strong, whilst the average direct cotton dyestuff has no affinity for wool below 40° C. ; in fact, many will not dye the wool at still higher temperatures.

The dyeing of wool and silk goods to a solid shade is essentially a matter of temperature, always supposing that the dyestuffs being used are recommended as suitable for this particular purpose. The reason for this is that whilst both acid and direct cotton dyestuffs have a strong affinity for silk at low temperatures, coupled with a weak affinity for wool, the position is exactly reversed at high temperatures in that the dyestuffs boil off the silk on to the wool. Within these two extremes there is a mean temperature at which the affinity for

both fibres is equal. The mean temperature of the following
acid dyestuffs shows that this varies within wide limits :

Quinoline Yellow (C.I. 801) ..   ..   ..   60° C.
Orange IV (C.I. 143) ..   ..   at boil
Fast Red (C.I. 176)   ..   ..   40° C.

Temperature, however, is not the only determining factor, but
structure of the cloth also plays a part in determining the
temperature at which the dyestuff should be dyed to obtain a
solid shade, e.g. a hard twisted, crossbred yarn will naturally
be dyed a heavier shade than a loosely spun botany yarn at the
same temperature. The requisite judgment on these points can
only be obtained by actual experience, and such experience is the
necessary qualification of a foreman dyer.

In actual dyeing it follows, therefore, that dyeing is com-
menced cold, and the dyeliquor gradually raised to the correct
temperature for the particular dyestuff being used. If the
wool is lighter in shade than the silk the temperature must be
raised to get the wool heavier, conversely if the silk is lighter the
temperature must be lowered. In dyeing compound shades, it is
essential to choose dyestuffs which have the same temperature
for giving solid shades, or else the task will be extremely difficult.
Fortunately, there are many direct cotton dyestuffs which dye
the wool and silk a solid shade between 90° and 100° C., and
these are excellently adapted for giving solid shades. These
dyestuffs give particularly favourable results in many instances
if dyed in a soap bath : they are specially suitable for pro-
duction of browns, greens, olives, etc., whilst the Coomassie
Navy Blue class of dyestuffs is excellently adapted for blue and
navy shades in a neutral bath.

Cotton or Viscose Rayon and Silk Unions.—Mixtures of
silk with viscose rayon are so similar in dyeing properties to
silk and cotton mixtures that they may be considered as one
general type of union. Temperature coupled with the correct
choice of dyestuffs is again the deciding factor in the dyeing of
this class of material which may require to be dyed in two-colour
or solid shades. Two-colour effects are obtained by first dyeing
the silk with acid dyestuffs which do not stain cotton, then filling
up the cotton in a fresh bath with basic or direct cotton dyestuffs.

For this latter purpose a very careful choice of dyestuffs must be made, because, as already indicated, many direct cotton dyestuffs have a pronounced affinity for silk at low temperatures. There are, however, some which have but a weak affinity for silk at low temperatures, amongst which may be mentioned direct cotton blues of the " B " and " FF " types, cotton blacks of the " BH " type, Mikado and Stilbene dyestuffs and Benzo Fast Scarlets.

Filling up the cotton is carried out with the addition of Glauber's or common salt, soda ash, and soap ; the addition of the two latter helping to keep the dyestuff off the silk. The temperature to which the bath is raised varies with the different dyestuffs. " BH " blacks should not be taken above 40° C., but " FF " sky blues may be taken much higher without staining the silk.

Solid shades on cotton and silk unions are dyed on similar lines to those adopted in the dyeing of wool and cotton unions.

Wool and Cotton Unions.—The oldest type of union material consists of wool and cotton. This class of union is usually dyed by one of the following methods :

    (*a*) Dyeing the wool with acid dyestuffs, and then filling up the cotton in a cold alkaline bath with direct cotton dyestuffs (Burl dyeing).

    (*b*) Dyeing the wool with acid dyestuffs, mordanting the cotton with tannic acid, fixing with tartar emetic, then dyeing the cotton cold with basic dyestuffs.

    (*c*) Dyeing the material in a neutral Glauber's salt bath with dyestuffs which dye solid shades ; or by a combination of acid dyestuffs which dye the wool in a neutral bath, leaving the cotton undyed, and direct cotton dyestuffs which dye the cotton more than the wool.

    (*d*) Dyeing the cotton in the warp with cotton dyestuffs which are fast to cross-dyeing, then dyeing the weft in the piece with acid dyestuffs.

    (*a*) This method is usually carried out with goods in which it is not of much importance that the cotton should be of exactly the same shade as the wool so long as it is covered ; this is the method commonly used in shoddy dyeing, the cotton being afterwards filled up by means of sumac and iron in the case of

blacks, blues, and heavy browns, or with some suitable direct cotton dyestuff depending on the shade of the wool. It is also used in pile fabrics with a cotton warp back, and for goods that are likely to crimp if dyed in a neutral Glauber's salt bath. Its advantage is that brighter shades on the wool are obtained by this method than by the single-bath method. For filling up the cotton a large range of direct cotton dyestuffs are available which leave the wool unstained at low temperatures whilst having a strong affinity for cotton. The dyeing of the cotton should not be carried out absolutely cold, because experiment has shown that the temperature of dyeing has a very distinct influence on the fastness to rubbing of the dyestuff on the cotton. The higher the temperature at which the filling up is carried out, the faster to rubbing is the dyed cotton ; thus, if the filling up is carried out cold the cotton will be liable to rub, but if carried out at 50°–60° C. it will be found quite fast to rubbing ; moreover, the higher the temperature employed the better the value obtained from the dyestuffs. This operation is usually carried out on the washing machine, which enables a very short liquor to be used, and in which the heavy roller plays an efficient part in squeezing the dyestuff into the centre of the material. As assistants 1 lb. Glauber's or common salt and 2 oz. soda ash per 10 galls. liquor are used. This method has a great advantage over the older method of sumac and iron with subsequent shading with basic dyestuffs. The shade of the wool was always flattened, whilst the final shade also rubbed due to the basic dyestuffs.

(*b*) The wool is dyed in the usual manner with acid dyestuffs, washed well, mordanted with tannic acid, fixed with tartar emetic, then dyed with basic dyestuffs.

This process is very long, and requires no less than four distinct baths, and at least four washings, but despite this drawback, its use is indispensable for solid shades of bright pinks, greens, blues, and violets. It is also the method frequently employed for the production of shot effects.

Katanol W (Resistone, Taninol) is a product possessing properties which make it of special value in the dyeing of half-wool and half-silk fabrics. It possesses the property of reserving the animal fibres in such goods, thus preventing the cotton dyestuffs from staining the wool or silk. At the same time

it imparts to the cotton an affinity for basic dyestuffs, and since it requires no fixing bath it has this additional advantage over tannic acid. Katanol W is therefore particularly suitable for obtaining two-colour effects, since it permits of a higher temperature being employed for filling up the cotton with direct cotton dyestuffs. In addition the shade of the wool or silk remains clearer whilst the higher temperature which may be used increases the productivity of the direct cotton dyestuffs.

(c) Single Bath or Neutral Bath Method.—Owing to the introduction of many more dyestuffs suitable for this process the adoption of this method has largely increased. Though it is still impossible to obtain certain bright shades such as vivid greens, pinks, and violets by this method, a constantly increasing range of shades may be obtained, notably blacks, blues, browns, khakis, greens, reds. For the purposes of single-bath union dyeing dyestuffs may be classified as follows :

1. Acid dyestuffs which possess a good affinity for wool (and silk) in a neutral bath, so that they may be used for shading the wool in union dyeing. A very large number of acid dyestuffs have practically no affinity for wool in a neutral bath, and are therefore useless for this purpose. A reasonable number are, however, suitable, amongst which may be mentioned :

Acid violets.	Coomassie Red.
Rhodamine B.G.	Citronine Y (C.I. 145).
Acid Blacks.	Wool Red R.
Fast Red (C.I. 176).	Milling Yellow HG.
Orange II, IV.	Polar Reds.
Coomassie Navy Blues	Elite Fast Yellow 2G.
(C.I. 289.)	Carbolans.
Gloria Blacks.	Elite Fast Reds.
Coomassie Blacks.	

2. Direct cotton dyestuffs which in a neutral bath give practically a solid shade on wool, silk, and cotton fabrics.

3. Direct cotton dyestuffs, which in a neutral bath dye the cotton much heavier than the wool. These may be made to yield solid shades by the judicious use of formic or acetic acid.

By using combinations of the above three classes of dyestuffs, solid shades may easily be obtained after a little practice. One or two examples will suffice to illustrate the method. There is no direct cotton navy which will give a solid shade on wool, silk, and cotton, therefore one must use a mixing or buy it ready mixed by the dyestuff manufacturer. Direct Black BH dyes the cotton a full navy, whilst only staining the wool and silk a dirty grey. A navy blue is wanted which will dye the wool and silk in a neutral bath ; the Coomassie Navy Blue class of blue does this, so the requisite percentage is found out by a dye-test. Should the shade be a little flat on the wool, then some Acid Violet is added to brighten the shade.

Again, there is no direct cotton violet which will give a solid shade on wool, silk, and cotton : all dye the wool redder than the cotton. This redness of the wool and silk may be corrected by using a blue shade acid violet, which will dye the wool and silk only.

The successful application of this method depends largely on the intelligent appreciation of the two following cardinal points :

(1) The use of as concentrated a dye-liquor as possible.

(2) Careful regulation of temperature.

(1) The usual amount of liquor employed is 200 gallons of water for 100 lb. material ; if more liquor is taken, then proportionately more dyestuff will be required.

(2) The temperature requires to be carefully regulated owing to the fact that cotton has the greater affinity for the dyestuff below the boil, whilst the wool has the greater affinity at the boil. It is therefore possible, by regulating the temperature, to control the shades of the wool and cotton within certain limits. If the wool is not heavy enough, work at the boil for a short time ; on the other hand, if the cotton is not heavy enough, shut off steam and allow the cotton to feed in the cooling bath. When the difference in the shade is too great to be corrected in this simple way, recourse is had to shading with suitable dyestuffs. If the wool has to be corrected, add an acid dyestuff which possesses a good affinity for wool in a neutral bath, and work at the spring boil ; if the cotton has to be corrected, shut off steam and add a direct cotton dyestuff which has a much greater affinity for

cotton than wool, and work in the cooling bath. It is absolutely essential in this class of work that the cotton be slightly heavier than the wool, so that the cotton does not stand out prominently ("stare" is the term often used) when the shade is examined. There are two methods of working employed in practice :

(1) Start cold, raise to the desired temperature in half an hour, dye for half an hour, shut off steam, and allow to feed in the cooling bath for half an hour.

(2) Start at the boil, work 20–30 minutes at the gentle boil, shut off steam and work half an hour in the cooling bath.

Both the above methods are used, but the authors prefer the former owing to the fact that the cotton is well covered before the wool begins to take up the dyestuff. No hard-and-fast rule can be laid down as to the length of time to keep the dyeliquor simmering. This must be left to the judgment of the individual dyer, since so much depends upon the nature of the wool, the twist of the yarn, and the weave and design of the material. In general practice, however, it may be laid down that vigorous boiling is rarely required, because the wool will usually take the dyestuff to the desired extent at the spring boil. An exception must be made in the case of pale shades, when it will be necessary vigorously to boil the dyeliquor in order to get the dyestuff on to the wool, because many dyestuffs which yield a solid shade in a full percentage without being boiled, require to be boiled when dyed in a pale shade in order to get the dyestuff on to the wool. Even with vigorous boiling it will sometimes be found necessary in these cases to add an acid dyestuff with a good affinity for wool in a neutral bath in order to bring the wool to the shade of the cotton. Except in pale shades the baths are not exhausted and may be kept for subsequent lots.

The following varieties of union material require to be specially mentioned.

Union Felt.—This material must be dyed as quickly as possible, because it is very liable to stretch in the hot liquor. The winch must also be fixed as near the surface of the liquor as possible so as to reduce the drag on the cloth to a minimum.

Mohair Pile Fabrics.—If the goods have been curled it is not advisable to employ the single-bath method, because in the hot neutral liquor the curled portions become straight again. This curled class of goods is, therefore, usually dyed with acid dyestuffs, the cotton, jute, or linen warp either being dyed prior to weaving with dyestuffs fast to acid cross dyeing or it is suitably backed when made up into rugs, mats, table-cloths, etc. If the pile is not curled, then the goods may be dyed in a single bath ; since the warp does not show it is only essential that it is dyed darker than the wool, but it need not be exactly the same tone as the wool. Glauber's salt should be reduced to a minimum and the fabric, when washing off, soured with a little acetic acid.

Union Hose is probably the most difficult of all half-wool material to dye, because, when stretched as in actual wear, the slightest difference in tone between the wool and cotton at once becomes very noticeable. The matching of the shade on the wool and cotton requires to be very accurate. Moreover, a combination of dyestuffs which will give a solid shade on one quality of union hose will not always give the same result on a different pattern. Great experience is therefore required by the dyer of this class of material.

Shades of Union Goods Fast to Milling and Washing.— The after-treatment of direct cotton dyestuffs with formaldehyde and bichrome as described in Section VI. is of great importance in the dyeing of fast to milling and washing shades on union goods. Fast washing blacks have been largely dyed by this process on union waste and angola yarns for a number of years, and navies to a lesser extent.

Similar fast shades of olives, greens, browns, and drabs may be dyed by using dyestuffs which are suitable for after-treatment with chromium fluoride as detailed in Section VIII. More recently a series of dyestuffs, the Benzo Fast Copper dyestuffs, has been introduced for dyeing cellulose-wool materials in one bath in conjunction with selected copper-resistant Metachrome or fast acid dyestuffs in shades fast to light and washing. Dyeing is carried out in presence of Glauber's salt by the usual method employed with the Metachrome or fast acid dyestuffs, and the dyeing then after-treated with copper sulphate and acetic acid at 60° C. so as to develop the Benzo Fast Copper dyestuff. A

similar series of dyestuffs, the Coprantine dyestuffs, are being developed at the present time. In dyeing these dyestuffs the material is entered at 50°–60° C., raised to the boil in $\frac{1}{2}$ an hour, and dyeing continued at the boil for $\frac{3}{4}$ to 1 hour. An amount of Coprantine salt I equal to the weight of dyestuff is then added, and dyeing continued for $\frac{3}{4}$ of an hour at 80° to 90° C. to develop the shade and fastness. These dyestuffs give shades having good fastness to light and washing.

Shoddy Dyeing.—In many cases it is found necessary previous to dyeing to strip the dark-coloured shoddy in order to obtain a suitable ground for the desired shade. The method of stripping is carried out in various ways. Amongst those commonly employed the following may be mentioned.

(*a*) Work for half an hour at 40°–60° C. with 5–10 per cent. soda ash, then wash well.

(*b*) Boiling with 5–15 per cent. sulphuric acid for half an hour ; this is frequently effective in cleaning the piece, especially if the shoddy was originally dyed with wood dyestuffs. Previous to dyeing, the pieces should be well washed to remove excess of acid. If they are subsequently to be dyed by the one-bath method they must be effectively neutralized with soda ash in order to prevent the dyestuff striking on to the wool and therefore leaving the cotton uncovered.

(*c*) Boiling with 3–8 per cent. sodium bichromate and 6–12 per cent. sulphuric acid ; this gives very good results, stripping the material to a medium brown bottom, which may be made lighter by a subsequent slight stripping with hydrosulphite.

(*d*) Hydrosulphite is now frequently used for stripping purposes and is very effective in all cases except where the shoddy was originally dyed with indigo ; in this case the goods will look stripped in the bath owing to the hydrosulphite reducing the indigo, but on washing off the material the indigo oxidizes up again. In cases where indigo is present the bichrome and acid treatment is the most effective. As mentioned above, hydrosulphite is frequently used after stripping with bichrome to make the bottom still lighter. In all cases the stripping is

carried out in an alkaline bath at 50°–60° C., which gives a better handle to the goods than if they are stripped at the boil, though this temperature may be employed if the shoddy is difficult to strip. After stripping and washing, the pieces must be soured with D.O.V., otherwise the pieces are very liable to come out flecky. Hydrosulphite used to be commonly made for this purpose by the dyer himself. For this purpose sodium bisulphite and zinc powder are required, the hydrosulphite being made by stirring 13 oz. zinc into every gallon of bisulphite used. The liquid heats up as the zinc is stirred in, and stirring is continued till the original smell of the bisulphite has disappeared, when the bisulphite is said to be " killed." It is allowed to settle, and the clear liquid drawn off and used. No more hydrosulphite should be made than is required for immediate use, because it decomposes on standing. Hydrosulphite in a solid and stable form is now on the market and has largely supplanted the use of bisulphite and zinc owing to its greater convenience.

Basic zinc hydrosulphite formaldehyde is put on the market for stripping shoddy under various names such as Zinc Formosul and Decroline. This is insoluble and is applied as follows : charge a dyebath at 60°–70° C. with $1\frac{1}{2}$–$2\frac{1}{2}$ per cent. formic acid (80 per cent.), enter the material, then add 2–5 per cent. Zinc Formosul, raise the temperature to the boil and boil 15–30 minutes. The acid gradually dissolves the zinc-hydrosulphite so that there is less loss than when using the less stable sodium hydrosulphite.

The dyeing of pieces containing a cotton warp with shoddy weft is usually carried out in one of the three following ways :

(1) Stripping and dyeing in the same bath.
(2) Dyeing the weft with acid dyestuffs, then filling up the cotton on the washing machine with direct cotton dyestuffs or with sumac and iron.
(3) Single-bath method of union dyeing in a neutral Glauber's salt bath.

1. In this process the goods are first boiled with the bichrome and sulphuric acid for a quarter of an hour, steam is shut off, and an acid dyestuff is salted in, steam put on again, and the piece

dyed to shade. The shades that are usually obtained by this method are olives, browns, and drabs, which are somewhat near the brown bottom obtained by stripping alone, *i.e.* where only a small quantity of dyestuff to change the stripped bottom to the desired shade is required. The cotton is treated with a small quantity of sumac, then with iron liquor, and finally shaded with Bismarck Brown, Chrysoidine, or Auramine, or it may be filled up with direct cotton dyestuffs. This is done cold with the addition of Glauber's or common salt and soda ash, using 1 lb. salt and 2–4 oz. soda ash per 10 gallons liquor. The amount of liquor employed should be as small as possible, and as the baths are not exhausted, the liquors may be kept for subsequent pieces. The filling up of the cotton should be carried out on the washing machine because the constant squeezing through the heavy rollers ensures the piece being penetrated. It may be here noted that pieces in which the cotton is filled up with direct cotton dyestuffs do not rub like those in which the cotton is shaded with basic dyestuffs ; again the shade of the wool is not altered to the same extent as when the cotton is filled up with sumac and iron ; the latter, however, adds weight to the pieces.

The necessity of shading the cotton to the exact shade of the wool depends largely on the weave of the piece. If the cotton warp is well covered, so long as the cotton is stained the shade is not of much importance ; in cases where the cotton shows on the surface of the cloth it is necessary to match the shade of the wool exactly or the cloth will have a mottled appearance.

2. In this method the weft is dyed with acid dyestuffs and the cotton is subsequently filled up in the manner described in the previous method.

3. This method of dyeing in one bath with the addition of Glauber's salt and soda ash has its limitations, but whenever it can be employed it will be found considerably cheaper owing to the less time required, thus saving labour and increasing the output. The shades which are successfully dyed on the large scale by this method are blacks, browns, drabs, and fawns, scarlets, reds, bordeaux, and some shades of navy blue and green. When using the one-bath process the necessity of thoroughly neutralizing the cloth if it has been stripped cannot be too strongly emphasized, because if the cloth contains any acid the dyestuffs

strike rapidly on the wool, leaving the cotton bare.   The following points should also be borne in mind : the less liquor employed the less dyestuff is required, and vice versa, because, except in light shades, the dyebath is never exhausted.   For the same reason steam-coils are better than steam-pipes.   The cotton takes the dyestuff below the boil, whilst the wool covers better at the boil.   When boiling, therefore, the baths should not be vigorously boiled, but should be kept at the spring boil.

The dyer is thus able to control the shade within certain limits by regulating the steam.   If the wool is heavy enough but the cotton thin, shut off the steam and allow the cotton to feed in the cooling bath.   If the bath is on the alkaline side, it favours the better covering of the cotton.   In fact if the pieces have been stripped and neutralized it is advisable to add 1–2 per cent. soda ash to the dyebath to ensure that the bath does not become acid owing to the goods being imperfectly neutralized, whilst it also counteracts the property of shoddy that it more readily takes up dyestuff than wool which has not been previously dyed.

Mixture effects are obtained by leaving the shoddy its original shade and staining the cotton on the washing machine in a cold alkaline liquor with some suitable direct cotton dyestuff.

Wool and Viscose Rayon Unions.—Ever since viscose rayon became an established fibre it has been used in conjunction with wool mainly for effect threads, the rayon being usually dyed with fast to cross-dyeing dyestuffs prior to weaving and the wool subsequently piece dyed.   In more recent years viscose rayon in the form of staple fibre has been introduced and is being increasingly used in conjunction with wool.   This latter development has led to the extensive examination of methods for the dyeing of such unions by one-bath methods, since, although the most satisfactory results are obtained by dyeing the fibres separately and then blending, the general use of such a method is more expensive than the one-bath method, and tends to off-set some of the economy obtained by the use of the rayon staple. It is beyond the scope of this volume to detail all the methods which have been examined and the reader is referred to a paper on this subject by Robinson (*J.S.D.C.*, 1938, p. 312), where twelve possible methods for the dyeing of solid shades on wool-viscose unions are detailed.   In general, where a high degree of fastness

is not required the dyeing of wool-viscose unions is closely similar to that of wool-cotton unions described on p. 293.

Fast solid shades may be obtained on wool-viscose staple fibre union fabrics by first padding the material at 60° C. in an aqueous solution of a Soledon dyestuff, followed by drying, and steaming in moist steam at 100° C. for 30 mins. and finally developing in an acid persulphate bath for 3 mins. at 95° C. (see I.C.I., Gleed and Thomas, E.P. 478,663).

Cotton and Viscose Rayon Unions.—A large number of types of unions of cotton and viscose are produced nowadays, the cotton being used both in the unmercerized and mercerized forms. These unions embrace, amongst others, sateens, voiles, lingerie, hosiery, and furnishing fabrics. All these fabrics may require to be dyed in solid shades by one-bath methods, with direct cotton dyestuffs, when the fastness requirements are not high, or with sulphur, developed, azoic, or vat dyestuffs when the fastness requirements are more severe. The fundamental difficulty when dyeing such materials is that the rayon usually dyes more strongly than unmercerized cotton, and the methods employed for the production of solid shades on such materials are designed to obtain dyeing conditions which minimize the affinity of the rayon as will be seen later.

(a) *Direct Cotton Dyestuffs.*—In dyeing unmercerized cotton and viscose rayon materials in solid shades with direct cotton dyestuffs the controlling factors are temperature of dyeing, and the quantity of salt added to the dyebath ; the conditions needed for maximum solidity· being low temperatures and minimum salt addition. Providing suitable combinations of dyestuffs are used, pale shades, if they are dyed without salt, do not present much difficulty. Heavy shades, however, present serious difficulties and the production of, for example, a uniform dark navy blue, a bottle green, or a nigger brown is practically impossible since the conditions giving maximum solidity are the reverse of those required to produce such heavy shades, namely high temperatures and large salt additions. The best conditions are to dye at 60° C., and to use the minimum quantity of salt. If hosiery has to be dyed, low temperatures cannot be adopted since penetration of the seams would not be obtained in a cool dyebath. For satisfactory results a boiling dyeliquor has therefore to be

employed and the dyeing allowed to proceed in a cooling liquor containing either no salt or the minimum quantity which is required to produce the desired shade. Black shades do not present much difficulty providing a non-bronzing black is used, as the cotton can be dyed a full enough shade to tone with the heavier shade of the rayon. In the case of materials containing mercerized cotton and viscose rayon the position is the reverse to that obtaining with unmercerized cotton and viscose rayon unions, since in the former case the affinities of the two fibres are more balanced than in the latter case. With these unions it is easier to produce solid dark shades than solid pale shades : the conditions of dyeing giving the best results being elevated temperatures and the addition of large amounts of salt. The correct choice of dyestuffs also plays an important part in obtaining satisfactory results.

(b) *Sulphur Dyestuffs.*—Faster shades may be obtained with the sulphur dyestuffs than with the direct cotton dyestuffs, but they are seldom used, as high percentages of dyestuff are required to produce the required shades and matching to shade is difficult. As with the direct cotton dyestuffs the dyeing temperature is kept low, and the minimum quantity of salt is used.

(c) *Azoic Dyestuffs.*—The Naphtols are usually applied to cotton and viscose unions on the padding machine. As the substantivity of all Naphtols, excepting Naphtol AS–BR, is lower at high temperatures than cold, the impregnation is usually carried out near to the boil. With Naphtol AS–BR the best temperature is at 30°–50° C. Development is also usually carried out on the padding machine, and to allow complete coupling to take place the goods after squeezing are given a few air passages.

(d) *Vat Dyestuffs.*—As with the direct cotton dyestuffs the vat dyestuffs when normally applied tend to dye the viscose rayon a heavier shade than the cotton. This is particularly so with blues and greens, the difficulty of producing solid shades being greater with heavy shades than with light shades. In most cases, however, saleable results are obtained providing the two fibres are dyed tone-in-tone which is only made possible by the correct choice of dyestuffs. Dyeing at low temperatures and salting the dyestuff on to the fabric gives more solid shades with certain weak alkali vat dyestuffs, but this method cannot be

regarded as being altogether satisfactory. Probably the best all-round method for the production of solid shades on these unions is the pigment padding process (see p. 208), but this method is limited to light and medium shades. Like the vat dyestuffs the solubilized vat dyestuffs dye the rayon a heavier shade than the cotton, and their use can only be suggested for pale shades.

Unions Containing Acetate Rayon.—When acetate rayon was first produced commercially one of its most serious initial handicaps was its lack of affinity for the dyestuffs commonly used in dyeing cotton and regenerated cellulose rayons. The solution of the problem of dyeing acetate rayon which was ultimately reached opened out the possibility of obtaining in conjunction with cotton and the other rayons a series of cross-dyeing or solid effects which has since developed into one of the largest outlets for acetate rayon. Raw silk has also found considerable use in conjunction with acetate rayon, particularly in the production of suede crepes in which the rayon is delustred in the piece by treatment with boiling soap solution. It is necessary, therefore, to consider separately the dyeing of these two types of acetate rayon unions.

Acetate and Cellulose Fibre Unions.—Unions of acetate rayon with either cotton or regenerated cellulose rayon can be satisfactorily dyed in solid shades, in two colours, or either fibre may be reserved. In producing solid shades direct cotton dyestuffs and dispersed acetate dyestuffs are used in the same dyebath together with a little soluble oil to keep the acetate dyestuff well dispersed, and salt to exhaust the direct cotton dyestuff. In dyeing such unions the temperature of the dyebath is usually raised from 40°–80° C. for bright finishes and to 100° C. for dull finishes during $1\frac{1}{2}$ to $2\frac{1}{2}$ hours, or still longer with heavy shades such as nigger browns, wines, etc. One of the principal factors to observe in these cases is the effect of artificial light on the combination used, as otherwise marked differences in shade will be observed depending upon the lighting conditions. For the production of blacks it is preferable to use in the same dye-bath a developed black for the acetate rayon and an ordinary direct cotton black for the rayon or cotton, and then to develop with B-hydroxynaphthoic acid. Contrasting shades can, of course, also be dyed by the method outlined above. The unique

dyeing properties of acetate rayon have made it possible for manufacturers to keep stocks of woven fabrics in the grey, and to then obtain any two-coloured or solid effects by dyeing.

Although it was soon found that direct cotton dyestuffs had practically no affinity for acetate rayon, many of them did produce unwelcome stains on the rayon. These stains were really due to impurities in the dyestuffs : for instance, it is quite easy in making direct cotton blacks of the EW type to use an excess of one of the end components, viz. : meta-phenylenediamine which produces a yellow stain on acetate rayon. The dyestuff manufacturers, however, soon overcame this difficulty by placing on the market batches of dyestuffs which had been specially tested for freedom from staining of acetate rayon. These specially purified dyestuffs are used particularly when it is desired to leave the acetate rayon white.

The viscose rayon or cotton may also be reserved, but as all cellulose acetate rayon dyestuffs stain these fibres more or less, a clearing treatment is desirable, especially when dyeing heavy shades. A method which has proved successful with diazotized and developed blacks is to treat for $\frac{1}{2}$–1 hour at 80° C. with 0·5–1 per cent. sodium hydrosulphite and 0·1 per cent. soap (on weight of material) prior to diazotizing and developing. According to Tomlinson (*J.S.D.C.*, 1936, p. 376) the most effective clearing results are obtained by treating for 15 minutes in a cold or lukewarm bath with 0·025 per cent. solution potassium permanganate and 0·05 per cent. solution concentrated sulphuric acid : shades other than blacks require 0·1 per cent. solution potassium permanganate and 0·1 per cent. solution sulphuric acid. The treated goods are then rinsed and treated in a cold bath with 0·1 per cent. solution sodium bisulphite and 0·1 per cent. concentrated sulphuric acid.

Vat dyestuffs can be applied to cotton or viscose rayon in unions with acetate rayon without damage to the latter by vatting with caustic soda and sodium hydrosulphite, adding sufficient phenol or B-naphthol to convert the caustic soda to the phenate or B-naphtholate and dyeing at about 40° C.

Acetate and Silk Unions.—With acetate and silk unions the silk is usually woven or knitted in the gum, and degummed in a boiling soap solution, which treatment removes the lustre from

the acetate rayon. These unions are usually dyed by the one-bath method either for two-colour effects or for solid shades with dispersed acetate dyestuffs and either neutral-dyeing acid dyestuffs or direct cotton dyestuffs. Suitable dyestuffs are chosen with due regard to their reserving effect on the other fibre. As acetate dyestuffs generally stain silk to a greater extent than they stain cotton or viscose rayon the two-colour effects obtained on acetate and silk unions are usually rather less contrasting than on cotton or viscose rayon unions.

Garment Dyeing.—Modern garment dyeing may be said to have been made possible by the introduction of the acid and more particularly direct cotton dyestuffs, because it is with these two classes that the satisfactory results now obtained are produced. Prior to the introduction of union blacks, garments were dyed with logwood black, and the full process took five days, whereas it is now possible by use of union blacks for a garment to be dyed black and returned within twenty-four hours. Garment dyers are unique in the variety of fabrics which they handle, making a wide knowledge of all classes of dyestuffs, coupled with a complete knowledge of fabrics, essential to success. No two garments received are alike in their structure or history. They may consist of silk, wool, cotton, and rayon, all on the one garment. To add to the difficulty, the natural silk may be weighted and the rayon may be of two or more varieties which reflect themselves in the different ways they take the dyestuff. In fact, practically all materials made up into articles of wear or furnishings have to be handled. The treatment of leather and the re-dyeing of cellulose acetate rayon are two branches of garment dyeing which have been developed in the last few years. Moreover, the garments as received are frequently dirty, stained, faded, and in many cases tender, so that it is impossible to dye them without damage or shrinkage. It will thus be seen that though a garment dyer is often rather contemptuously referred to as a " job dyer," garment dyeing is in reality a most difficult section of dyeing.

The task of the garment dyer has always been complicated by the effect of exposure to light on the garment to be re-dyed, and the problem of covering fades is still one of the major difficulties experienced.

The Dyeing of Faded Garments.—The term " faded gar-

ment " has a double meaning to the garment dyer. A garment may have been dyed with a fugitive dyestuff, which has faded so quickly that the atmospheric influences have not had time to attack the fibre. Such a garment presents no difficulties to the intelligent garment dyer, because he is able to strip the dyestuff and make a satisfactory job of the garment.

Another garment may be dyed with fast dyestuffs, but the fibre itself may have been badly " burnt " by the sun and atmosphere combined, especially about the shoulders ; covert coatings are a good example. In many cases it is impossible to dye such a garment any shade other than black, which is the garment dyer's salvation, because fades usually cover up in black, and do notshow like they do in green, navy blue, and brown shades.

This problem of covering the latter type of fades is not as general with other fibres as it is with wool, since dress fabrics are seldom worn until the fabric is really damaged, and with cotton and rayon dyed with vat dyestuffs the fabric is worn out in most cases before the need for re-dyeing occurs.

It is an interesting speculation as to what happens to the wool fibre during the exposure. If the exposure is at all prolonged the surface fibres become very brittle, and by brushing the exposed portions with a strong brush all the surface fibres may be brushed away, leaving the fabric very bare. The same thing happens in a dyed faded garment ; if the surface is scraped with a knife the wool underneath is found to be dyed the normal shade.

Recent work by Race, Rowe, Speakman, and Vickerstaff (*J.S.D.C.*, 1938, p. 141) has shown that the damage sustained by wool fibres during exposure to light and air, either during growth or in garment form, is due to hydrolytic attack on the cystine linkage between the peptide chains which results in the exposed wool losing sulphur and containing an excess of sulphydryl and carbonyl groups. This change in the chemical composition of the wool naturally has an effect on its dyeing behaviour. Thus it has been shown that in consequence of disulphide bond breakdown, exposed fibres swell to a greater extent than unexposed in acid or alkaline solution, and are, therefore, more accessible to colloidal dyestuffs, so that the exposed parts are dyed darker than the unexposed in such cases. With crystalloidal dyestuffs on the other hand, the primary dyeing may be

level, but later becomes unlevel owing to the greater ease with which dyestuff is stripped from the strongly swollen exposed parts, resulting in lighter shades on the exposed parts.

Every conceivable remedy was tried without success to cure this trouble, so that garment dyers could only rely on choosing dyestuffs which experience had shown gave the best results in practice. If the job came out too bad to return, the dyer usually suggested that it should be dyed black, which, as already stated, covers up the fades.

More recently, Race, Rowe, and Speakman (*J.S.D.C.*, 1938, p. 159) have shown that by treatment with chromium acetate the difference between exposed and unexposed wools, as regards swelling, is considerably diminished with the result that level dyeing is promoted. The optimum conditions given to promote both level acid and after-chrome dyeings are to treat the material with 3 per cent. chromium acetate and 4 per cent. glacial acetic acid at 40° C. for ½ hour, the liquor-wool ratio being 50 : 1. All forms of chromium acetate are not effective, the best results being given by a basic chromium acetate that dissolves in water to give a violet solution (*J.S.D.C.*, 1939, p. 82). The use of a standing bath is undesirable (*J.S.D.C.*, 1939, p. 261). Chromium salts of mineral acids have been shown to be ineffective, as are the chromium salts of organic acids stronger than acetic (*J.S.D.C.*, 1939, p. 86).

Wet Dyeing.—In the main the garment dyer employs two methods of dyeing, viz. :

1. Dyeing the wool and silk in an acid bath with acid dye-stuffs and filling up the cotton in a subsequent bath with direct cotton dyestuffs.

2. Dyeing in a neutral bath with a combination of dyestuffs suitably chosen to give a solid shade.

Both methods have their advantages, but the second process is the quicker. This method is often termed " soft dyeing," as contrasted with the acid method. The first method is commonly used for goods which are badly faded, as this method gives the best result on faded goods and enables brighter shades to be dyed on bad grounds than is possible by the second method. Black is naturally the most important shade for a garment dyer, and is usually dyed by the single-bath method. For this purpose

union blacks ready mixed by the dyestuff manufacturer are used, and they are dyed with the addition of Glauber's or common salt. As assistant in the dyebath many dyers prefer to use common salt to Glauber's salt, as they claim the former does not soften the goods like the latter. This has been shown by experiment to be due to the fact that a solution of Glauber's salt becomes alkaline whilst hot, but becomes neutral again on cooling, whilst a hot solution of common salt remains neutral. It is the alkaline condition of Glauber's salt whilst hot which produces this softening of garments which has been noticed by practical garment dyers.

When dyeing garments by the neutral-bath process, care should be taken that the garments are not acid, which would cause the dyestuff to rush on to the wool to the detriment of the cotton. We have met several garments, especially in dress goods, which have been in an acid condition. The reason is because experience has shown that if the wool is left slightly acid after dyeing, the shade is less likely to rub than when neutral or if left alkaline. Dyers of dress goods, therefore, often send out their goods slightly acid.

The desirable properties for a union black to have are as follows :

1. It should work for months in a standing bath without deterioration of shade.
2. It should not bronze.
3. Its shade should be bloomy, so that it may give a good black on bad bottoms.
4. It should possess great covering power.
5. It should be non-alkaline, so that it does not soften the garments.

In practice the dyeing is carried out by two methods, either of which gives good results, so that the choice of method must be left to the individual dyer.

1. Dye three-quarters of an hour at 90° C.) with the addition of 10 per cent. salt.
2. Enter at the boil, dye 20 minutes at the boil, shut off steam and dye 30–40 minutes in the cooling bath, 10 per cent. salt being used as assistant.

The general methods for the dyeing of cellulose acetate

unions have already been detailed earlier in this section, so that they need not be repeated here.

Dry Dyeing.—This is the misleading term given to the dyeing of garments in a benzine and methylated spirit bath. It is employed for dyeing delicate made-up silks, etc., which cannot be unpicked, but which would be damaged if dyed in water. It is a difficult process to carry out, but has been much improved of recent years. Farrell published an interesting paper on this subject in *J.S.D.C.*, May, 1908, to which the reader is referred for full details.

The following is one method used on the big scale. First, make a benzine soap as follows: saponify 4 gallons oleic acid with $\frac{3}{4}$ gallon ammonia (22 per cent.), then add 20 gallons benzine. Make $\frac{1}{2}$ per cent. solution of the dyestuff in methylated spirit, and allow the salt, etc., in the dyestuff to settle, then pour off the clear solution—all the dyestuffs do not dissolve perfectly clear, but do so when added to the benzine soap. This solution of dyestuff will mix in any proportion with the above benzine soap. The depth of shade obtained depends upon the strength of the solution and length of time of dyeing; after dyeing, the shades may be washed in benzine without loss of depth.

All the basic dyestuffs are soluble in methylated spirit, but preference should be given to those acid and other dyestuffs which are sufficiently soluble in methylated spirit for this purpose. Several members of the sulphonated triphenylmethane class are suitable for this purpose, such as Acid Violets, Acid Greens, Disulphine Blues, etc., whilst Spirit Induline and Nigrosine are also used.

Section XVI.—THE EVALUATION AND IDENTIFICATION OF DYESTUFFS

The evaluation of dyestuffs is a much more difficult task than many people realize, since evaluation includes not merely comparative money value tests, but also the determination of dyeing and fastness properties. By the introduction of new auxiliary products—some of which depreciate the fastness to light of many dyestuffs—the number of necessary tests has had to be extended ; similarly, new finishing processes make additional demands, *c.g.* the Trubenizing process requires that the shades used in collar fabrics should not bleed in acetone.

Few people so exhaustively test a dyestuff as is necessarily carried out in a dyestuff manufacturer's experimenta ldyehouse, because a dyestuff manufacturer offers his dyestuffs to all dyestuffs consuming trades, whilst individual dyers confine their tests to the well-defined limits of their own trade. Nevertheless, there remains many important properties of dyestuffs upon which information is still not published. The golden rule of dyeing demands that compound shades should be dyed with dyestuffs which dye on at the same rate. This necessitates a knowledge of the rate of exhaustion of the individual dyestuffs, whilst it is also necessary to determine the salt sensitivity of direct cotton dyestuffs. Such information is particularly useful when dyeing by the pack method; without it satisfactory results can only be obtained by the expensive method of blind working and elimination. Publication of such details has for the most part been made by the manufacturers of the synthetic fibres in order to enable the best possible dyeing results to be obtained on their products.

Methods for the volumetric and gravimetric estimation of dyestuffs have been developed from time to time. Thus Knecht and Hibbert (" New Reduction methods in Volumetric Analysis," 1925) devised a ·volumetric method using titanous chloride,

whilst Trotman and Frearson (*J.S.D.C.*, 1931, p. 344) have suggested the gravimetric estimation of certain dyestuffs using alkaloids. These methods may be of value in special circumstances but they cannot substitute actual dyeing tests since no purely volumetric, gravimetric or colorimetric method can determine if dyestuffs penetrate equally or exhaust at the same rate, knowledge of which is absolutely necessary for practical dyehouse work. The use of a colorimeter is, however, a very convenient method for obtaining quantitative data regarding the dyeing behaviour of dyestuffs when dyed under various conditions. This may be exemplified by reference to the tables of time of half-dyeing (p. 252), percentage exhaustion (p. 257) and sensitivity of salt data (p. 258) of direct cotton dyestuffs which were obtained by combined dyeing tests and colorimetric estimations.

When testing dyestuffs in the laboratory efforts should always be made to imitate as closely as possible the actual conditions used in the dyehouse ; exact imitation is, however, frequently impossible. The same liquor to material ratio, and the same time and temperature of dyeing should be used, whilst the dyestuff should be tested on the fibre on which it is to be used—it is misleading to test a dyestuff on cotton if it is to be used on viscose rayon, as the rate of dyeing will be different on the two fibres. When making comparative dyeing tests the conditions of temperature or vigour of boiling must be uniform in all the dyepots. To this end a bath with a suitably perforated lid may be used. The bath should be charged with a solution which can be heated to a temperature of 120°–130° C. which will ensure that the dyeliquor in the dyepots will actually boil when this is necessary. Calcium chloride is both cheap and effective for this purpose, whilst sodium nitrate may also be used. Calcium chloride solution has one drawback in that in cold weather it sets into a solid mass which may crack the bath, whereas sodium nitrate falls in fine crystals. Glycerol has also been used, but this should be avoided owing to its objectionable smell on continual heating. Some people use plain water baths which make it impossible for the dyeliquor in the dyepots to boil : dyetests carried out in such a bath may be misleading, especially with alizarine and chrome dyestuffs. Steam heating is more economical than gas heating, as steam at 60 lb. pressure in a 2-in. copper coil will

keep a bath containing 15 dyepots of 750 cc. capacity boiling with only one-eighth of a turn of the valve. The dyepots used for small tests should be of porcelain, enamelled iron, Monel metal, or stainless steel; the metal pots are more economical as they are proof against the clumsiness of the average laboratory boy. Cracked porcelain or enamelled dyepots should never be used, as any dyestuff which penetrates into the cracks, and which cannot be removed by cleaning, is liable to contaminate subsequent dyeliquors and so vitiate any dyeings made in such dyepots.

When testing a dyestuff against a standard it is absolutely essential that a dyeing of the standard should be made every time the dyestuff is tested, because a slight variation in the conditions of dyeing is sufficient to vitiate the tests from a comparative point of view. This is a point which is frequently overlooked. Again, old solutions of the standard dyestuff must never be used as certain dyestuff solutions, *e.g.* Chlorazol Fast Orange G, tend to gel on keeping, and do not give the same colour value as is given by freshly made solutions.

In carrying out tests of a dyestuff, account must always be taken of the average percentage which is used in practice. It is far more sensible to test a direct cotton Sky Blue at $\frac{1}{4}$ per cent., than at 2 per cent., because a $\frac{1}{4}$ per cent. shade is the one more often dyed. On the other hand, Fast Chrome Blacks should be tested at 6 per cent. rather than 1 per cent., because a 6 per cent. shade is more frequently dyed in practice. As the strength of a shade is, however, more easily judged in a weak shade than in a strong shade, providing the dyestuff is homogeneous, it is advisable to dye a 1–2 per cent. shade of a black for strength, and a full shade to determine the tone of the black and its fastness properties.

In cases when it is necessary to know whether a dyestuff is a mixture, the following tests may be used. If the dyestuff is soluble in water a small quantity is blown from the end of a spatula on to wet filter paper; after a minute or two the components of a mixture dyestuff may be readily seen by examination of the filter paper. It should be noted that many dyestuffs contain shading dyestuff added during standardization. As the quantity of shading dyestuff used is generally small no difficulty

is experienced in differentiating such dyestuffs from mixtures deliberately built up from different dyestuffs. Vat and sulphur dyestuffs may be similarly examined by blowing them on to paper wetted with caustic soda and sodium hydrosulphite or sodium sulphide solutions of dyebath strength respectively. Another method which is sometimes used with both water soluble and water insoluble dyestuffs is to dust a little of the dyestuff. on to the surface of concentrated sulphuric acid in a porcelain basin ; dyestuff mixtures show different coloured streaks in the acid. Acetate dyestuffs may be examined by blowing a small quantity on to a paper saturated with acetone or some similar solvent for these dyestuffs.

In making dyeing trials of the various classes of dyestuffs the following points should be particularly noted.

Basic Dyestuffs.—The chief properties to determine are solubility, fastness to washing and perspiration and, on cellulosic fibres, the amount of tannin or sulphurized phenol (Katanol, Resistone, Taninol) required as mordant to give the brightest and fastest shades. For methods of mordanting, see p. 89.

Acid Dyestuffs.—For dyeing trials on wool a liquor to material ratio of 30 : 1, and on pure silk, a ratio of 50 : 1 are suggested. In the first trial using 1 per cent. dyestuff, dyeing should be started cold, the temperature raised to the boil in $\frac{1}{2}$ hour, and boiling continued for a further $\frac{1}{2}$ hour. Three such dyeings should be made using 2 per cent. acetic acid, 2 per cent. formic acid, and 2 per cent. sulphuric acid as assistants. The rate of dyeing should be noted, as if the dyestuff dyes on quickly it will usually dye unlevel, whereas if it dyes on slowly as the temperature is raised, and still dyes on slowly at the boil it will be a level-dyeing dyestuff. If it does dye on too quickly and, therefore, unlevel with the amount of acid used, the acidity of the dyebath should be reduced and the best conditions for dyeing the particular dyestuff so worked out. Small pieces of cotton or rayon should also be placed in the dyebaths, and the staining of the cellulose noted. This is necessary in order to determine whether the dyestuff stains effect threads.

Acid dyestuffs required to dye wool and cotton unions in solid shades by the one-bath method in conjunction with direct cotton dyestuffs should be dyed from a neutral dyebath containing

Glauber's salt, and the value obtained by this method compared with the value obtained by dyeing from an acid dyebath. The nearer the two dyeings are in depth the more suitable is the dyestuff for neutral dyeing.

The ease of levelling of acid dyestuffs may be tested by the following methods :

(a) Prepare a boiling dyebath with a small percentage of the dyestuff and 5 per cent. sulphuric acid—no Glauber's salt—and dye a piece of tightly woven cashmere cloth in the dyebath for 15 minutes at the boil. Compare the result with a dyestuff of known excellent levelling properties which has been dyed under identical conditions at the same time.

(b) Prepare a dyeing of the dyestuff of the same depth of shade as an acid dyestuff of known excellent levelling properties. Place each dyeing together with an equal weight of undyed wool into separate blank acid dyebaths and boil. Note the degree of transference from the dyed to the undyed material after different periods of time.

(c) A variation of (b) is to prepare a dyeliquor for 10 grams of wool, divide the dyeliquor into two equal portions, and to dye 5 gms. of wool for 15 minutes at the boil in one half. Then mix the divided dyeliquors together and dye the dyed wool and a further 5 gms. of undyed wool in the mixed dyeliquors for $\frac{3}{4}$ hour at the boil. Examination of the dyed patterns will indicate whether the dyestuff has good levelling properties or not, since the two pieces will be equally dyed by a levelling dyestuff. A dyestuff of known good levelling properties should also be dyed at the same time under the same conditions.

The penetrating power of an acid dyestuff is best tested by dyeing a piece of closely milled hat felt in a boiling dyebath for $\frac{1}{2}$ hour, cutting the dyed felt in half and comparing the degree of penetration with a known suitable dyestuff.

The suitability of a dyestuff for salting, *i.e.* adding to a boiling dyebath for shading purposes, may be tested as follows : Assume, for example, that a red dyestuff is being examined. A piece of cloth or yarn is dyed with 0·1 per cent. Quinoline Yellow, 0·1 per cent. Disulphine Blue V, and 3 per cent. sul-

phuric acid for $\frac{1}{2}$ hour at the boil. 0·1 per cent. of the red dye-
stuff is then added and boiling continued for a further $\frac{1}{2}$ hour.
After washing and drying the material is examined for evenness
and penetration, when if it is satisfactory from both points of
view it may safely be used for salting purposes. In all cases an
accepted standard dyestuff must be dyed at the same time under
identical conditions. Other properties to note are fastness to
light, washing, perspiration, milling, decatizing and carbonizing.

Mordant Dyestuffs.—These dyestuffs should be tested by
the three methods detailed in Section VII., *i.e.* by the metachrome
process, by the after-chrome method, and on a chrome mordant,
taking care to test on all the forms of chrome mordant given
therein. The properties to note are solubility, fastness to
decatizing, rubbing, potting, levelling, milling, light, and sen-
sitiveness to metals.

Direct Cotton Dyestuffs.—These dyestuffs should be dyed
in presence of common salt using a liquor to material ratio of
twenty to one, cold, 40° C., 60° C., 80° C., 90° C., and at the
boil, and the affinity noted at the different temperatures, because
if a dyestuff has a good affinity at low temperatures it will be
useful for mixed materials and burl dyeing. Exhaust tests
should also be made in order to ascertain if the dyestuff exhausts
well or not, and thus determine if it will be necessary to work it
in a standing bath. Assuming the dyestuff is a black, exhaust
tests are carried out as follows : Prepare a dyebath with 6 per
cent. black, $\frac{1}{2}$ per cent. soda ash, 30 per cent. salt. Enter the
cotton at 40° C., raise to boil, and boil $\frac{1}{2}$ hour, wring out the
cotton, returning the liquor to the dyebath, then make up the
volume of the dyebath to the original volume, add 10 per cent.
salt, but no dyestuff, and dye in it for $\frac{1}{2}$ hour at the boil an equal
weight of cotton to that originally taken. This second test is
what is called the exhaust test, and shows how much dyestuff is
left in the dyebath. The direct cotton dyestuffs vary very much
in the amount they leave in the dyebath (see p. 258). When a
colorimeter is available the degree of exhaustion may be quan-
titatively determined by comparing the suitably diluted exhaust
liquors with a dilute solution of known strength of the same
dyestuff.

In the case of direct cotton dyestuffs required for the dyeing

of rayon the tests detailed in Section XIII. should also be made, whilst dyestuffs required for pack dyeing should be examined in a liquor to material ratio of ten to one for rate of exhaustion and salt sensitivity (p. 257).

The properties of these dyestuffs to which attention should be paid are fastness to light, washing, acids and hot-pressing; levelling should be tested on similar lines to those given under acid dyestuffs (p. 316). The effect of anti-crease finish on light fastness should also be borne in mind.

Sulphur Dyestuffs.—The first thing to determine is the proper amount of sodium sulphide required to give the best results. Dyeing trials should be carried out with varying amounts of sodium sulphide, using common salt as an assistant. Exhaust tests should be carried out as detailed under direct cotton dyestuffs.

The dyeing of sulphur dyestuffs on the small scale is exceedingly difficult, and the results so obtained are never as good as those obtained on the large scale. In making comparative dyeings great care must be taken to see that all the dyeings are treated exactly alike, so as to ensure that they oxidize under similar conditions. To this end the patterns should be plunged straight from the dyebath under cold water, washed off together, squeezed together, and dried together. It is no use comparing dyeings of one hank which has been allowed to hang on a peg in the wet state for 15 minutes before drying with one which has been dried immediately. Owing to the fact that all dyeings of sulphur dyestuffs oxidize on storing, it is advisable to treat with sodium perborate or bichromate all dyeings which are made to match dyed patterns, otherwise the newly made dyeing will not be comparable with one which has been dyed some time; even these precautions do not produce the same effect, as is shown by an old dyeing.

The properties which should be specially noted are fastness to light, milling, washing, and cross-dyeing. Sulphur blacks should also be tested for their liability to cause tendering on storage (p. 153).

Azoic Dyestuffs.—Naphtols, bases and fast colour salts should all be examined for solubility and naphtols for substantivity; dyeings of these dyestuffs should be tested for change of

shade on soaping, light, rubbing, cross-dyeing, and bleaching. If the dyeings are on rayon they should also be examined for " blinding " (see p. 183).

Vat Dyestuffs.—These dyestuffs should be examined for the ease with which they may be vatted and for their affinity at different temperatures. Levelling tests should be made by method (*b*) described for the acid dyestuffs, using blank caustic soda and sodium hydrosulphite vats instead of blank acid dye-baths at the temperature at which the dyestuff is to be used, *e.g.* 60° C. If it is customary to use a restraining agent when dyeing vat dyestuffs the effect of the restraining agent should be examined as this usually varies with the particular dyestuff used. Special tests for the suitability of a vat dyestuff for the dyeing of rayon are described in Section XI.

The fastness of the dyestuff to light, boiling, washing, cross-dyeing, and bleaching should also be examined ; if the dyestuff is required for dyeing casement shades it should be tested for its liability to accelerate tendering on exposure to light and atmospheric influences (see p. 199).

Acetate Dyestuffs.—These dyestuffs should be examined by the tests described in Section XIII., and for the staining of viscose rayon and cotton effect threads. As certain yellow and orange acetate dyestuffs are phototropic, for example, Setacyl Direct Yellow 2R, they should be examined from this point of view. (A phototropic dyestuff is one that fades or changes shade on exposure to daylight, but regains its original shade on being kept in the dark for some time.) A suitable method for the examination of the phototrophy of an acetate dyestuff is as follows : A grey shade is dyed using the yellow or orange in combination with Duranol Red 2G and Duranol Blue G, or other known non-phototropic dyestuffs, the dyeing wound on to a card, and stored in a drawer overnight with one half covered. The card is then exposed to direct sunlight for 15 minutes, and examined. If a change of shade has occurred the card is again stored in a closed drawer and from time to time compared with the unexposed portion to see if the original shade is eventually restored. Acetate dyestuffs should also be tested for fastness to gas fumes, light, washing, and perspiration.

Fastness Tests.—On the question of fast and loose dyestuffs,

it is necessary to grasp the fact that there is no such thing as absolute fastness as applied to dyestuffs, yet one is repeatedly asked in the course of business if a certain shade is absolutely fast and such terms as " guaranteed fadeless " are used by many firms who apply this guarantee even to the direct cotton dye-stuffs.   It is essential to realize that fastness is purely relative and not absolute.   If experience has proved that a dyestuff during the lifetime of a fabric withstands all the influences to which that fabric is subjected, then the dyer can designate that dyestuff as fast for that particular class of goods.   The range of fastness for which dyers have to cater is extraordinarily wide and varied, and it is this fact which makes all terms of fastness as applied to dyestuffs purely relative.   This may be illustrated by choosing two extreme instances.   A lady's dance frock is never exposed to daylight, and the only process through which it may be passed is dry-cleaning; therefore, the most fugitive dyestuffs may safely be termed fast for such fabrics.   On the contrary, a naval uniform is exposed to the severest weather conditions extant, viz.: sunlight and exposure to sea air; therefore, the fastest obtainable dyestuffs must be used for this purpose.

One is justified in saying that the nearest approach to absolute fastness is made by some of the modern vat dyestuffs, in that some will last longer than the fabric on which they are dyed, *i.e.* the fabric perishes before the shade has faded, yet these dyestuffs will not withstand boiling under pressure with caustic soda without bleeding on to adjacent white.

These examples suffice to show that in considering the fastness. of dyestuffs it is always necessary to lay down two conditions, viz.:

1. For what purpose is the fabric on which the dyestuff has to be dyed to be used.

2. To what processes is the dyestuff required to be fast.

It is no use putting good and, therefore, expensive dyestuffs on to cotton cloth which is going to be used for pocketings ; on the contrary, it is no use putting dyestuffs not fast to washing into shirtings.

It follows logically from this that different sections of the dyeing industry have entirely different standards of fastness which apply to their respective sections only.   This explains why different dyers hold such widely different views of the fast-

ness of one and the same dyestuff. The dyeing industry is necessarily essentially commercial, so that price is the ruling factor, from which it follows that for the dyeing of shoddy cloth which is sold at 3s. a yard a much lower grade of dyestuffs must be used than those used in dyeing the best worsted overcoatings which will sell at 30s. a yard. From the above it will be seen that the terms " fast " and " loose " are purely relative in the dyeing industry.

Again, fashion and modern custom have an important influence on the class of dyestuff consumed. Some fashionable garments are so ephemeral that they are discarded before the dyestuff has been put to a severe test. People now buy cheaper clothes more often rather than expensive clothes at long intervals, so that great fastness is frequently neither looked for nor expected. Both of these factors increase the consumption of the less fast and cheaper dyestuffs.

The following are some of the fastness tests through which dyeings of a dyestuff may be put.

Light.—In making light fastness tests regard must be taken of the use to which the dyed fabric may be put and the probable location of its exposure. For instance, it is no use making a severe exposure of a direct cotton dyestuff which is to be used for linings which will never be exposed to light. On the other hand, a dyestuff which is to be used on suitings should have at least one month's summer exposure ; dyestuffs which withstand such an exposure will be found to be sufficiently fast for the average lifetime of the suit. Cloths for sailors' uniforms which must withstand continuous and unusually severe exposures are frequently nailed to the mast during an out-and-home journey to Australia, or other extreme measures are taken, such as exposure at the end of a pier for six months without protection. Exposure at the seaside or in country districts is much more severe than is exposure in an industrial district owing to the differences in the intensity of the sunlight in such localities. For the same reason, the comparative number of sun hours in different districts recorded by sun recorders are often misleading. Such instruments usually simply record the presence of sunlight, but do not give any indication of its intensity.

Comparative light exposures must be made using dyeings of

the same depth of shade because the fastness of a dyestuff depends upon the depth of shade exposed. The following method of exposure has been successfully used for a number of years and gives valuable information on the effect of depth of shade on the fastness of a dyestuff. Eight shades of increasing depth of shade are wound on to a card, one-half covered, and exposed under glass in a closed ventilated frame mounted at 45° to the vertical. The dyeings may be kept clean during the exposure in an industrial district by placing the card in a cellophane envelope, as the use of such an envelope has been found to have no effect on the rate of fading of the dyestuff.

As certain dyestuffs accelerate the fading of other dyestuffs in compound shades this fact should not be overlooked when adopting a new dyestuff. Thus Oxyphenine accelerates the fading of most direct cotton reds and certain direct cotton greens when these are exposed in compound shades. Again, green shades produced from a vat yellow like Paradone Yellow GC and Caledon Blue RC fade yellow, in spite of the fact that in self shades the blue is considerably faster than the yellow.

The fastness of a dyestuff is also influenced in many cases by the fibre upon which it is dyed. Thus Malachite Green is considerably faster when dyed upon unmordanted cellulose acetate rayon than when dyed upon viscose rayon or cotton. It is, therefore, necessary to make light exposures of dyestuffs on the fibre on which the dyestuff is to be used.

As the light fastness of many dyestuffs is adversely affected when the dyed fabric is anti-creased, i.e. treated with a solution of a semi-condensate of urea and formaldehyde (methylol urea), and subsequently heated to convert the semi-condensate into a water insoluble condensation product, dyestuff makers have issued lists of dyestuffs showing the influence of this treatment on their light fastness. Similarly a reduction in light fastness is also found as a result of the after-treatment of dyed materials with cation-active auxiliary products (see Section XVII.).

Although, whenever possible, light fastness should be tested by an outside exposure, this is not possible during the winter months in this country, and it is, therefore, necessary to use fading lamps as a substitute for sunlight. When using these lamps it should be remembered that the rate of fading of dye-

stuffs depends to a very large extent on the temperature and humidity of the air at the surface of the pattern. The higher the humidity the quicker the fading, so that only lamps in which the humidity can be controlled should be used. At the present time there are marketed three fading instruments, each of which has, as its light source, an enclosed carbon arc. These are the Fadeometer, the Fugitometer, and the C.P.A. Fading lamp. The original Fadeometer was unsatisfactory on account of the low humidity and the high temperatures produced. This defect has been overcome in the new type. Forty patterns may be exposed in it simultaneously, and 90 hours' exposure will give a distinct fading with most direct dyestuffs, and 200 hours' with the less fast vat dyestuffs. The Fugitometer is a similar instrument to the Fadeometer and holds 32 patterns. Control of temperature is obtained by a fan of variable speed, and of humidity, by means of a pump which circulates humidified air over the patterns. Thirty-two. patterns may also be exposed in the C.P.A. Fading lamp under controlled temperature and humidity conditions. The novel feature of this instrument is that the patterns are mounted on a rotating holder to equalize the distribution of the light. For a fuller description and critical examination of fading lamps, see " Report of the Society of Dyers and Colourists Fastness Committee " published in 1934. Hunter (*J.S.D.C.*, 1940, p. 64) has described an accelerated light fastness test developed and used by the British Cotton Industries Research Association at the Shirley Institute. The light source is a high intensity arc which, when its light has passed through glass to remove short wave ultra-violet radiation, gives a light which in quality very closely resembles daylight, and in intensity may be made to exceed that of noon summer sunlight twenty fold. The equipment in use at the Shirley Institute can test 32 exposed samples of the highest commercial fastness in a week of five days at six hours per day, whereas a plain carbon arc of the Fadeometer type working all day and all night for five days a week requires about four weeks for the same purpose, whilst the exposure required to daylight would be more than a year.

About twenty years ago the first efforts were made to standardize the fastness to light of dyestuffs. At that time the Fastness Committee of the Association of German Chemists

perhaps better known as the " Echtheitskommission," published
the first scales intended to standardize the fastness to light of
dyeings on wool and cotton, which were followed later by scales
on silks and rayons. There was no relation, however, of the wool
types to the cotton or silk types, and therefore the fastness
figures on the various fibres could not be compared with each
other. Attempts were then made to adjust the scales on the
individual fibres so that they gave comparable figures. This
met with little success as it was soon recognized that the process
of fading depends upon a number of factors, particularly the
humidity of the air, and that the influence of these factors
varies with the fibres used. The Fastness Committee of the
Society of Dyers and Colourists decided from the results of a
large amount of experimental work on different fibres carried
out by Cunliffe (*J.S.D.C.*, 1930, p. 108) that wool was the
fibre least sensitive to humidity and other atmospheric
influences. They, therefore, confined their work to the production
of suitable light standards on wool only. In 1932 the German
Fastness Committee chose eight type-dyeings on wool, the fastness
to light being standardized by " 1 " denoting the lowest and
" 8 " the highest fastness to light. Two series of standards,
a red and a blue one, each comprising seven dyeings of increasing
fastness, numbered 2 to 8, and graded so that each member of
the series was approximately twice as fast as the preceding one,
were adopted in 1934 by the Society of Dyers and Colourists
Fastness Committee. Attempts were then made to obtain
international agreement on light fastness standards by inviting
comment and establishing contact with similar Fastness Com-
mittees in Germany and America ; considerable progress was
made, but complete agreement had not been reached when war
broke out. An improved set of standards, consisting of 8 blue
dyeings only, the parallel red series being abandoned as super-
fluous, have recently been published (*J. Text. Inst.*, 1940, p. 513)
as " Tentative Standards for Fastness to Light" in accordance with
agreements made between the Society, the Textile Institute, and
between the latter and the British Standards Institution. At
first the fastness to light numbers were misused by the dyestuff
makers. Thus pattern cards were issued stating that a vat dye-
stuff had a light fastness of, for example, " 8 " whereas 8 in the

German Colour Fastness standard then represented 25 per cent. ·Indanthren Blue GCD Paste dyed under specified conditions on cotton, and unless all depths of the dyestuff marked " 8 " will withstand the same exposure it was not true to classify it as " 8." It was suggested, therefore (Whittaker, *J.S.D.C.*, 1932, p. 28), that the dyestuff makers should cease putting the " 8 " on their cards unless they stated the definite percentage of the dyestuff which is " 8." This criticism has now been met by the Continental dyestuff makers who in 1935 fixed the fastness to light of each dyestuff by three figures which refer to three depths of shade varying in the proportion of $1/3 : 1 : 2$. The dyeings prepared in depth 1 of all dyestuffs are chosen in such a way that they agree with each other in strength of shade and on all materials, with the exception of navy blue and black, the figures for which are given for fuller shades.

Washing.—It is a very common practice in making washing, scouring, and milling tests to plait the dyed yarn with white wool and cotton. The authors have strong objections to this procedure, since it is extremely difficult to wash out the last traces of soap and soda from the centre of the plait, so that when the plait is dried the residual soap and soda—as drying proceeds— becomes more and more concentrated, and the test amounts finally to heating the plait with strong soap and soda solution. The following method of making a washing test is very satisfactory. Make up a solution of 5 grs. soap and 3 grs. soda ash per 1,000 cc. of water. Use this solution at 40° C. for washing ; rub the material along with white wool, cotton and silk, between the hands for 15 minutes, allow to lie in the soapsuds for 15 minutes, wash off, first in warm water to remove the soap, then in cold water ; finally dry. Alkali is omitted if the test has not to be severe. Loss of depth, change of shade, and staining of white should be carefully noted as against standard. If knitted fabric is used the soap and soda may be easily washed out of the same ; moreover, it is also a very convenient way for subsequently mounting the tests in reference books. It should be noted that the Fastness Committee of the Society of Dyers and Colourists recommended in their report of 1934 the use of five red and five blue washing standards designed to cover the whole range of washing treatments of coloured materials from

domestic washing to severe laundry boils. A standard type of washing machine is recommended and four tests of increasing severity are prescribed (for details the report should be consulted). These standards are being further examined.

Scouring.—This test should be carried out by steeping the dyeing for six hours at 40° C. in 5° Tw. soda ash solution in presence of white wool, cotton, and rayon. Some standard shade should be fixed upon, and this should always be tested comparatively at the same time. The bleeding into the liquor, the loss in depth of shade, and the extent of the staining of the wool, cotton, and rayon noted in comparison with the standard, from which data the decision as to the fastness is made.

Milling.—This process is most satisfactorily tested by having the pattern stitched on to the end of a piece which will be given the necessary degree of milling, because this process varies widely according to the class of cloth and the particular finish required.

A convenient laboratory method consists of dyeing the dyestuff on yarn, and knitting it in a single thread hand-knitting machine, along with white wool, cotton, and silk, if necessary. This fabric is run through the rollers of a domestic wringing machine, which are driven from a shafting. Underneath the rollers is fitted a trough with an open steam-pipe in which soap and soda solution is put and heated to 40° C. Guiding bars are fitted in the trough so as to ensure that the fabric constantly passes through the soap liquor. Twelve years' experience of the machine has shown that a dyestuff which withstands the above test has never failed to stand in practical working. In this machine a dyestuff as fast to milling as sulphur black may be milled down to a grey in half an hour. A milled pattern must be examined for loss of depth, change of shade, and bleeding into adjacent white.

Failing the above, the pattern should be vigorously rubbed between the hands with strong soap and soda solution, then allowed to lie in the solution $\frac{1}{2}$ hour. Alternatively, the knitted pattern may be milled with hand-blocks.

Potting.—This is difficult to imitate in the small way, but the following method gives good comparative results, if a standard is always tested at the same time. Put a piece of the cloth to be tested between white flannel and cotton, wet them out thoroughly, then wrap them tightly round a glass rod and tie tightly round

PLATE 10
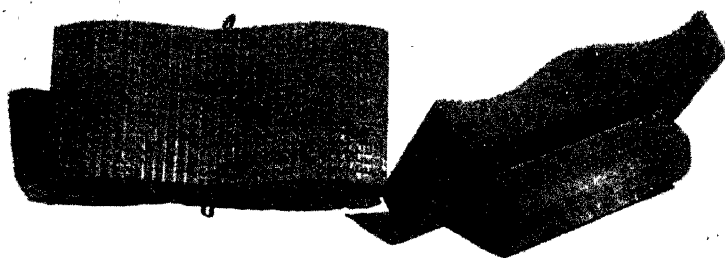
Hand Milling Blocks.

with string. Immerse the rod in water at the temperature at which the particular potting is carried out for the number of hours taken on the big scale. Note if the water is stained, also change of shade and staining of the white wool and cotton ; silk is also taken if necessary.

Decatizing.—This is a test which it is difficult to imitate on the laboratory scale, and is best carried out on the big scale when possible. Failing this, fit up a small perforated cylinder with the steam supply ; wrap this round with calico, blow the steam through till it is dry, then wrap on the pattern to be tested and blow the steam through the desired length of time.

Cross Wool Dyeing.—A skein of the dyed material is tied up with one-third of its weight of bleached cotton, wool and undyed viscose rayon, and the bundle scoured for 20 minutes at 40° C. in a liquor consisting of 1 per cent. soda ash and 0·5 per cent. soap solution, using a liquor to material ratio of 30 to 1, and then well washed off in cold water. The scoured material is then boiled for one hour in a 0·1 per cent. formic acid and 0·25 per cent. Glauber's salt solution, washed in cold water and dried. Change in shade of the dyed material and bleeding on to the other fibres is noted.

Stoving.—This is a test which is best carried out under the actual conditions under which the dyestuffs will be stoved in practice. Failing this, the following method gives good results. Stitch the dyed material between white wool and cotton, wet out thoroughly, then hang on a wooden stand or a glass plate, over which place a bell-jar. Put an iron box containing sulphur under the bell-jar and ignite the sulphur by dropping a red hot iron bolt in it. Allow air into the jar until the smell of sulphur dioxide is pronounced outside the jar, put the jar down and put putty all round the bottom to keep the jar gas-tight. Leave like this for 12 hours, wash off, dry, then examine the pattern for change of shade and bleeding into the adjacent white.

Cotton Bleaching.—The dyed yarn to be tested is stitched on to one end of a piece of unbleached calico which is then folded so as to enclose it, being finally folded lengthways and the ends tied together. This bundle is then treated for 2 hours at the boil in a 0·5 per cent. solution of soda ash, the volume being maintained by frequent additions of water; washed and treated in

sodium hypochlorite (2 gms./litre available chlorine) for one hour. It is washed, soured with 2 per cent. hydrochloric acid (37 per cent.) on the weight of material, washed and finally treated in 0·5 per cent. solution soap, plus 0·5 per cent. solution soda ash for 5 minutes at 90–95° C., washed off and dried. No change of shade or bleeding on to the calico should be noticed. Some shade changes are due merely to " over oxidization " during bleaching : such a shade may be restored by treating with cold 5 per cent. hydrosulphite in water, washing, and re-drying.

Carbonizing.—Soak the dyed wool along with some cotton for $\frac{1}{2}$ hour in cold sulphuric acid, 7° Tw., then squeeze out. Now place in a porcelain dish and heat for 1 hour at 80° C. when the cotton should be completely carbonized. Wash off, neutralize with soda ash, wash off, and dry. Compare the shade with some of the original pattern.

Effect of Metals.—Owing to the increasing adoption of dyeing machinery it is necessary to test for the effect of metals on dyestuffs. This may be done by making a dyeing of the dyestuff in a porcelain dyepot containing a piece of the metal and comparing the result with a dyeing made under similar conditions but without a piece of the metal in the dyepot. An exhaustive examination of the effect of metals upon dyestuffs has been made by Grundy (*J.S.D.C.*, 1929, p. 39 ; 1935, p. 377), and this work has been issued in booklet form by the Clayton Aniline Company under the title " Tabular Synopsis of the Action of Metals on Dyestuffs."

Perspiration.—It has recently been shown (" Report of the Society of Dyers and Colourists Fastness Committee ") that the earlier artificial perspiration solutions used for testing the fastness of dyeings to perspiration bore little resemblance to perspiration as shed from the human body. This was particularly so as regards the amount of sodium chloride used in these solutions. As a result of the analysis of human perspiration by Vass and McSwiney (*J.S.D.C.*, 1930, p. 190) the following solutions were recommended :

Acid perspiration liquor	*Alkaline perspiration liquor*
2·65 gm. NaCl per litre	0·839 gm. NH$_4$Cl per litre
0·75 gm. area per litre brought to pH 5·6 with N/10 acetic acid solution	1·732 gm. NaCl per litre
	0·424 cc. 0·88 NH$_3$ solution per litre, brought to pH 7·8 with N/10 acetic acid solution

The suggested method of testing is as follows :

" The test piece (1¾ in. × 2¼ in.) 4·5 cm. × 6·0 cm. and similar sized pieces of undyed neutral wool and cotton are thoroughly wetted in the artificial sweat solution (acid or alkaline). The test piece is then backed with the wool and cotton. The pad of materials so obtained is placed in the bottom of a chemically clean, flat crystallizing dish (4 in.) 10 cm. in diameter. Test liquor is then added to cover the materials. A smooth glass plate (3¼ in.) 8·25 cm. diameter weighing approximately 50 gm., is placed on the materials, and even pressure applied with three fingers. After the dish and contents have been left for 15 minutes at room temperature, the excess of liquor is poured off without removing the glass plate. The dish is then placed in the incubator at 37° C. for 4 hours. After this period of incubation, the materials are removed from the dish, separated and allowed to dry at room temperature. The materials are then inspected for bleeding. Any staining of the wool and cotton backings has been accepted as evidence that the pattern is not fast to perspiration. Alteration in tone of the pattern is not taken into account in assessing the fastness. It is realized, however, that gross alteration in shade may occur with some dyed patterns on treatment with the perspiration liquors. A dyed pattern showing a marked reaction of this character would clearly be unsuitable for human wear."

Hot Ironing.—Many dyestuffs change their shade temporarily under heat, particularly direct cotton dyestuffs. This test is simply carried out by placing a piece of wet cotton cloth over half the pattern and ironing it dry with a hot iron. Compare the ironed portion with the other portion immediately after ironing and when the pattern has cooled down and absorbed its lost moisture.

The change of shade of a dyestuff on heating is of considerable importance to the dyer as regards matching to pattern ; it is, of course, a defect and should be minimized by drying patterns wherever possible in a current of warm air, rather than on a hot metallic surface. The shade can be restored in many cases by steaming, but the worst offenders, *e.g.* the direct cotton violets, are liable on steaming to cool too far, *i.e.* absorb too much moisture so that the dyer must use his individual judgment in such cases.

In addition, it must be remembered that with such dyestuffs he is at the mercy of those rapid changes in humidity which are not uncommon in this climate. The dyer should, therefore, avoid the use of such dyestuffs, as far as possible, particularly in compound shades, but this is not always possible. Thus, for helio and violet shades, there is no alternative but to use direct helios which dry redder, or the vat helios which dry bluer. On the other hand, the use of these dyestuffs for the production of compound shades, *e.g.* greys, is to be deprecated, since in most cases other dyestuffs which are less changed on heating may be used.

Gas Fume Fading.—The fastness of dyeings to gas fumes may be tested by suspending pieces of the dyed material in a laboratory fume chamber above a series of Fletcher burners (see Rowe and Chamberlain, *J.S.D.C.*, 1937, p. 271). Part of the material should be protected from the action of the gases by being clipped tightly between cards, since this enables any change in shade to be more readily seen. Dyeings of a dyestuff known to be fast, and one which is not fast should also be exposed at the same time.

Trubenizing Test.—The dyed yarn is knitted as a narrow stripe with white yarn as the major portion of the knitting. A piece of cellulose acetate knitted fabric of similar size is placed inside the cotton knitting, the whole moistened with acetone and then ironed with a hot iron until the acetone has evaporated and the acetate fused. There must be no staining of the white by the dyed threads.

The Identification of Dyestuffs on the Fibre.—The dyehouse chemist is often asked to identify the type of dyestuff with which a fibre has been dyed. This is necessary if the dyehouse is asked to dye a bulk lot with dyestuffs of the same fastness as a pattern, and for which a dyeing price is wanted. Again, many customers choose shades for their cloths without any reference as to whether it is possible to reproduce these shades in the required fastness : for example, basic dyed patterns are often received which the customer requires of such a fastness that the use of vat or fast direct dyestuffs is necessary. In such cases it is generally impossible to obtain the same brightness with these dyestuffs, which usually necessitates submitting a dyeing of the nearest shade that can be given in the required fastness.

Identification by test enables one to report to the customer that the pattern has been dyed with dyestuffs which are not satisfactory for his purpose and this usually satisfies him to a greater extent than if the nearest possible shade were offered without any such comment.

It will be seen from the above that it is absolutely necessary to have a reliable scheme for the identification of dyestuffs on the fibre, as a mistake in identification may prove to be a costly one. Owing to the smallness of some patterns supplied to the dyehouse it is sometimes impossible to state with certainty the type of dyestuff with which a pattern has been dyed. In such cases there should be no hesitation in stating that the evidence is inconclusive, and a larger pattern should be asked for.

Recent developments in the finishing of fabrics have made it essential to be sure that the finish is not masking the reactions normally given by the various dyestuffs on unfinished fabrics. It is well known that the crease-resisting finish improves the fastness to washing of direct cotton dyestuffs, but it is not so well known that it interferes also in dyestuff identification. In submitting direct cotton dyestuffs on crease-resisted " Fibro " to the reduction test with caustic soda and sodium hydrosulphite at 90° C. reduction is considerably delayed ; Chlorazol Fast Orange AG on " Fibro " which normally strips in about half-a-minute takes about 5 minutes to strip. A dyeing of Diphenyl Fast Red 7BL on " Fibro " which, when boiled in presence of undyed " Fibro " for five minutes in a 0·2 per cent. salt solution, heavily dyes the previously undyed " Fibro " : given a crease-resisting finish little staining shows on the previously undyed " Fibro." The reduction of vat dyestuffs in NaOH and hydrosulphite at 90° C. is also delayed—thus Caledon Red BN on " Fibro " is reduced immediately with considerable loss in depth of shade, but when the dyeing is crease-resisted reduction takes about $1\frac{1}{2}$ minutes and there is little or no loss in depth of shade. Crease-resisting also masks the normal tests for sulphur dyestuffs ; no H_2S is evolved in the stannous chloride-hydrochloric acid test, whilst sulphur black is not destroyed as rapidly by means of hypochlorite. Again, crease-resisted basic dyeings, *e.g.* Malachite Green on a Katanol mordant, show much less bleeding in boiling ethyl alcohol.

Before making dyestuff identification tests on crease-resisted fabrics it is, therefore, essential to remove the finish by a treatment for 5-10 minutes at 90° C. with a 0·5 per cent. solution of hydrochloric acid which, in all the cases tried, has prevented interference with these tests.

Most of the above remarks apply to sthenosed " Fibro," *i.e.* anti-creased by formaldehyde treatment, the extent of the alteration depending upon the degree of sthenose given. Since such fabrics are appearing on the market, any fabrics suspected of having had this treatment should be given the acid treatment described above.

The increasing production of coloured pigmented rayon may also be puzzling to the inexperienced.

Several excellent schemes for the identification of individual dyestuffs have been published (see bibliography at end of this section) but as the majority of dyeings which have to be tested are compound shades of three dyestuffs and the dyer, in the majority of cases, only requires to know the class of dyestuff used to dye the pattern, such elaborate tests are only occasionally used in everyday work. The following simple tests make no claim to completeness, but are simply those which have been successfully used by the authors in routine work over a number of years.

Dyeings on Cellulosic Fibres.—In case of rayon patterns, determine if the rayon is acetate ; if so apply tests detailed on p. 338. If not, place the dyed pattern in a porcelain basin containing 1·25 cc. caustic soda 72° Tw. and 0·25 gram. sodium hydrosulphite powder conc. per 100 cc. of water so that it adheres to the side and is half immersed in the cold solution, which is then slowly heated and the colour changes noted.

Direct and Developed Dyestuffs.—Most dyeings of direct and developed dyestuffs are stripped with varying ease to a white by this treatment. Notable exceptions are direct dyeings on an Oxyphenine basis, and Primuline shades either chlorinated or developed, when the pattern either remains yellow or becomes yellow by the treatment. With some direct dyestuffs a colour change occurs which might be confused with the leuco compound obtained with vat dyestuffs. Thus, Chlorazol Fast Orange AGS dyeings when placed in the solution change in colour to a red-

violet shade, a change which can usually be noted even when the orange has been shaded with other dyestuffs to give fawn or brown shades. This colour change of some direct dyestuffs is distinguishable from the leuco compound of a vat dyestuff by the fact that the original colour cannot be restored by exposing to the air after washing the pattern in water ; moreover, if the pattern of a direct dyestuff is allowed to remain in the reducing solution it is eventually stripped to a white.

Direct and developed dyeings may be distinguished by the following tests : if a large pattern is available a washing test should be made side by side with a known direct and a known developed dyeing, and comparison made. Developed dyeings are in all cases faster to washing than direct dyeings of equal depth. Unfortunately, customers' patterns large enough to test for washing fastness are seldom available in practice, so that the following test has been developed for this purpose. A strip of bleached calico about 3 inches wide by 12 inches long is taken, and a piece of the pattern, together with pieces of known direct and developed dyeings, are placed separately on the calico. The calico is then folded over the dyeings, wetted with water, and dried with a hot iron. It is usually found that developed dyeings show very little staining of the calico, whereas direct dyeings show a well-marked staining depending on the depth of shade. Confirmation is obtained by reference to the known dyeings used as controls.

Vat Dyestuffs.—Patterns of these are usually reduced to characteristic leuco compounds of different hue to the original pattern which, if placed in an oxidizing bath, or washed and exposed to the air, are restored to the original shade. The leuco compound can frequently be seen bleeding from the pattern into the liquor, which is a characteristic indication of the presence of these dyestuffs, as those direct dyestuffs which show a shade change do not show such bleeding into the alkaline liquor.

Sulphur Dyestuffs.—Many sulphur dyestuffs—particularly blacks and blues—are reduced to characteristic leuco compounds.

The best method for the identification of sulphur dyeings is the stannous chloride-lead acetate test. This depends upon the fact that when sulphur dyestuffs are heated with a dilute hydrochloric acid solution containing stannous chloride sulphuretted

hydrogen is evolved and can be detected by means of lead acetate paper. The test is carried out as follows : A piece of the pattern (about 0·1 gram) is placed in a 6 in. $\times \frac{1}{2}$ in. boiling tube containing 2 cc. water, 2 cc. concentrated hydrochloric acid, and 0·2 to 0·5 grams. stannous chloride. The mouth of the tube is then covered with filter paper and one or two drops of lead acetate solution dropped on to the filter paper. The contents of the tube are then boiled for a few minutes (not less than three minutes), the filter paper removed, and examined. If the paper is stained brown or black the pattern has, in all probability, been dyed with sulphur dyestuffs. Care should be taken that too strong acid is never used, as the lead sulphide stain on the filter paper may be decomposed by hydrochloric acid given off if the contents of the tube are boiled too long. Whenever possible a control test should be done with a known sulphur dyeing using the same strength of acid.

Aniline Black.—This dyestuff gives a reddish brown leuco compound which may be confused with that given by a sulphur black. Aniline black may, however, be readily identified by placing a piece of the pattern into an evaporating basin, adding just sufficient strong sulphuric acid to char the fibre completely and diluting with cold water. A pale green solution, due to the formation of emeraldine, indicates the presence of Aniline black. A sulphur black topped with Aniline black does not give this reaction.

In order to distinguish between Aniline black, sulphur black, and sulphur black topped with Aniline black the pattern is placed into a sodium hypochlorite solution which has been heated to just below the boil. Aniline black goes red-brown, sulphur black is completely bleached, and sulphur black topped with Aniline black varies from a pale yellow to a brown depending upon the amount of Aniline black used in topping. By treating at the same time a pattern of sulphur black topped with a known amount of aniline, a rough estimate of the amount of aniline used may be formed with a little experience.

Azoic Dyestuffs.—These are, in most cases, stripped to a white or light yellow shade depending upon the combination used to produce the shade. With some combinations the stripping is extremely difficult, *e.g.* Naphtol AS-SW and Fast Red KB

base, and certain Naphtol AS-G combinations. If the stripping is done in a test tube in presence of an equal weight of undyed viscose rayon and the stripping liquor and the previously undyed viscose then examined in ultraviolet light the characteristic fluorescence of the Naphtol in alkaline solution is revealed.

Many azoic combinations are soluble in organic solvents, and this behaviour forms the basis of a confirmatory test for dyeings of such combinations. A piece of the pattern is placed either in a test-tube or on a spotting tile, and a little chloroform poured over it. A staining of the chloroform indicates that the pattern has been dyed with azoic dyestuffs. A negative result by this test should not be taken as conclusive, as some azoic combinations do not respond to the test, and reliance should be placed on the results of the other tests, particularly the examination in ultra-violet light. It is interesting to note that positive results are more often obtained with chloroform on cotton than on viscose, owing to the greater difficulty of clearing loose surface dyestuff from the cotton.

Basic Dyestuffs.—Many basic dyeings are immediately discharged by the alkalinity of the reducing liquor, and on washing in water or dilute acetic acid the original colour returns. Incidentally, such dyeings are usually discharged to a dirty grey or white by warm caustic soda solution alone ; and the original shade or a thinner version is restored by placing the discharged pattern into dilute acetic acid.

Basic dyestuffs are soluble in alcohol, so that in many cases when dyeings of these dyestuffs are boiled in alcohol the dyestuff is dissolved. If the alcohol is evaporated the basic dyestuff can be re-dyed, either on tannin or on Katanol mordanted yarn. If the dyeing is on a tannin mordant confirmation of the presence of a basic dyestuff may also be obtained by warming the pattern with ferric chloride solution and well washing with hot water, when the dyeing becomes very flat owing to the formation of the blue-black iron tannate on the fibre. It should be noted that the more general practice with viscose rayon is to dye the basic dyestuffs on a Katanol mordant and not on a tannin mordant. Several basic dyestuffs of the Resorcine type, like Eosine, Rhodamine, show a characteristic fluorescence when examined under

ultra-violet light, and this property may be used to confirm their identification.

Turkey Red.—Place the pattern on a spotting tile, disintegrate the fibres with strong sulphuric acid, and carefully drop strong caustic soda solution on to the mass. The characteristic violet colour of sodium alizaranate indicates that the pattern is dyed with Turkey Red.

If a dyeing of Turkey Red is boiled with titanous chloride the red immediately changes to a maroon ; this is very characteristic because other possible reds are usually stripped or in the case of vat reds reduced to the colour of their acid leuco compounds. Turkey Red when treated with a slightly acidified sodium hypochlorite solution is stripped in a short time, whereas most azoic reds withstand or are only slightly changed by this treatment.

Para Red.—Place the pattern between white calico and iron with a hot iron, or heat the pattern carefully in a test tube, when the colour volatilizes.

Dyeings on this dyestuff when treated with chloroform stain the chloroform a deep yellow colour.

Coloured Pigmented Rayon.—As the black is pigmented with Carbon Black it will give no reaction with any of the above tests. Other pigmented rayon yarns which have been examined by the authors showed no bleeding on to white when submitted to the wet hot ironing test (p. 333), and no change or loss in depth of shade when treated with caustic soda and sodium hydrosulphite (p. 332). These tests, therefore, serve to differentiate pigmented shades from the shades dyed by the normal methods after the yarn has been spun.

Dyeings on Animal Fibres.—Boil the pattern with ammonia when the average acid and direct cotton dyestuff will be stripped more or less completely. The solution is then evaporated down, a little common salt added, and a piece of cotton added. If the cotton is dyed, the pattern is dyed with a direct cotton dyestuff ; if it is not dyed, the pattern is dyed with an acid dyestuff.

Mordant Dyeings.—These are distinguished by their fastness to boiling ammonia.

The presence of mordant dyestuffs can be confirmed by

fusing some of the pattern with sodium carbonate and sodium nitrate in a crucible, dissolving the mass in water, acidifying with acetic acid, boiling to remove all carbon dioxide, and adding a solution of lead acetate, when a yellow precipitate of lead chromate proves the presence of chromium. Iron and copper may also be looked for.

Basic, vat and azoic dyeings can be tested for as described under " Dyeings on Cellulosic Fibres," p. 332.

Potting Blacks.—It is sometimes desirable to distinguish chrome blacks of the fast to potting and not fast to potting series. The following is a rapid means of doing so. Dilute concentrated nitric acid thirty times with water, boil the patterns for 2 minutes in this solution, and wash off immediately. Non-potting blacks are practically destroyed, whereas fast to potting blacks, owing to their superior fastness to oxidation, are not destroyed by this treatment.

Logwood Black.—Boil the pattern with a little dilute acid when the familiar red colouration will be given which when neutralized with ammonia changes to a violet colour.

Indigo.—Spot the material with concentrated nitric acid : pure indigo gives a bright yellow spot with a characteristic green rim. Many other dyestuffs will give a bright yellow spot, without the green rim characteristic of indigo. This test in the hands of an experienced operator is very good, but an inexperienced one may easily be deceived by shades which are faked up to give the indigo spot. The following two points help to enable the detection of faked shades, viz :

1. If the spotted fabric is allowed to stand 24 hours, the indigo spot does not deteriorate in shade, but the spot of a faked fabric usually does.

2. Pure indigo will give its characteristic spot with nitric acid of a lower concentration than the faked shade usually will. If one is suspicious of a fabric, then use nitric acid of as low a concentration as will give the characteristic indigo spot on a fabric known to be dyed with pure indigo.

Indigo may be sublimed off the fibre by gently heating it in a test-tube, the indigo condenses on the higher and cooler parts of the test-tube. This test requires practice.

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A very simple, yet effective, test for indigo on wool is to boil the wool with weak caustic soda until the wool is disintegrated ; after cooling down add a little hydrosulphite, when if indigo is present it will be reduced and form the characteristic yellow solution with bronzy scum, in fact, an indigo vat on a small scale.

Another simple test is to boil the pattern with strong sulphuric acid till the fibre is disintegrated, then dilute with water, when one gets a bright-blue solution of indigo extract. If the solution is masked by any bottoming or topping of the indigo, then dye a piece of wool in the solution, when it will be dyed the bright blue shade characteristic of indigo extract.

Dyeings on Cellulose Acetate Rayon.—The first test which should be made when identifying dyestuffs on cellulose acetate rayon is to decide whether the rayon has been saponified. This may be done by taking a few threads, dyeing at 80° C., with Sky Blue FF, and comparing the result with the untreated rayon. If the rayon has been saponified the shade will be definitely bluer than the original. Confirmation can be obtained by treating the rayon with acetone when unsaponified rayon will be completely soluble, whereas saponified rayon will not be completely dissolved.

Dyeings on unsaponified cellulose acetate should be tested as follows :

(a) Place a few threads of the dyed rayon together with a few threads of undyed unsaponified acetate rayon in a test-tube and heat in a 2 per cent. soap solution for 15 minutes at 80° C. Dyeings of the dispersion dyestuffs and the Solacets will stain the undyed rayon, whereas spun dyed rayon, coloured with pigments or Indigosols will show no staining. Azoic dyeings made by the one-bath method usually stain the undyed rayon to a yellow shade due to uncoupled Naphtol which when examined under ultra-violet light shows the characteristic fluorescence of the Naphtol.

(b) Place a few threads of the dyed rayon in a test-tube and treat for 10 minutes with a mixture of 40 per cent. methylene chloride and 60 per cent. benzene. The Dispersion dyestuffs will in most cases be completely stripped from the rayon, whereas the Solacets will stain the liquor but will not be completely stripped.

(c) Dyeings developed with b-naphthol or b-oxynaphthoic acid when treated with water containing a trace of alkali usually show the characteristic fluorescence of alkaline b-naphthol or alkaline b-oxynaphthoic acid when examined under ultra-violet light.

Dyeings on saponified rayon should be examined by the methods described for the cellulosic fibres (p. 332) for the presence of direct cotton, vat, and azoic dyestuffs.

REFERENCES

" Analysis of Dyestuffs," A. G. Green.

" The Identification of Vat Dyes on Cotton," J. I. M. Jones and W. Kilby, *J.S.D.C.*, p. 127, 1925.

" The Identification of Dyestuffs on Cellulose Acetate," C. M. Keyworth, *J.S.D.C.*, p. 343, 1927.

" Fur Dyes ; Their Oxidation and Identification on the Fibre," R. S. Forster and C. Soyhe, *J.S.D.C.*, p. 99, 1931.

" Reactionstabelle der Kupenfarbstoffe und Indigosole," E. Herzog, 1941.

" Identification of Dyes on Textile Fibres and Detection of Metals in Fibrous Materials, Dyes and Organic Pigments," E. Clayton, 1937.

" The Identification of Vat Dyes on Linen and Cotton materials (including the determination of the Dyeing class of all Dyes commonly found on such Materials," H. B. Bradley and D. A. Derrett-Smith, *J.S.D.C.*, 1940, p. 97.

Section XVII.—AUXILIARY PRODUCTS FOR TEXTILES

RECENT developments in textile chemistry have resulted in the appearance on the market of a number of products possessing diversified properties of interest to the dyeing and finishing industries to which the generic name of auxiliary or ancillary products has been given. It has been considered necessary to include a section dealing with these products in order to make this volume more complete.

One whose business activities are intimately connected with these products has stated that there are over 1,500 trade names of this class of product which are offered to the textile processing industries. These trade names do not necessarily represent 1,500 distinct chemical products, but they do illustrate the enormous development in textile auxiliaries which has taken place in recent years.

It will be appreciated that it is impossible to deal comprehensively with all the manifold uses of all these products within the limit of a section of this book. A full treatment would require a volume to itself. Therefore, it has been decided to deal with their general uses in dyeing and finishing. Proprietary names are only used as illustrations, and no effort has been made to give complete lists of allied products.

Anion and Cation-active Substances.—Many textile auxiliary products when dissolved in water behave as typical colloidal electrolytes, *i.e.* they react as if they consist of a number of giant polyvalent ions in equilibrium with the corresponding number of simple ions of opposite charge. Thus, although the sodium salts of the lower fatty acids behave as normal weak electrolytes· dissociating into simple anions and cations, with higher members of the series, *e.g.* the soaps, association begins to take place and colloidal character is assumed. The ion is no longer a discrete fatty acid anion but consists of an aggregate

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of fatty acid anion together with undissociated neutral salt molecules; it is a giant negatively charged polyvalent ion with an equal number of sodium ions in close proximity, and may be represented thus:

$$\left[\begin{array}{l} CH_3 . (CH_2)_n . COO \\ CH_3 . (CH_2)_n . COONa \end{array}\right]^- Na^+$$
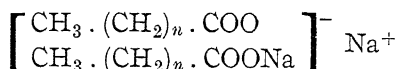
Compounds which, like the soaps, produce polyvalent ions carrying a negative charge are termed anion-active substances. Turkey Red Oil and the higher sulphonated oils such as Calsolene Oil, the Igepons, Lissapols, Ultravons, Gardinols, etc., are other typical anion-active substances; many dyestuffs, other than basic dyestuffs, also behave as anion-active substances.

Other auxiliary products, which are also colloidal electrolytes, form polyvalent ions carrying a positive charge; these are termed cation-active substances. Thus with cetyldiethylamine hydrochloride we have:

$$\left[\begin{array}{l} CH_3 (CH_2)_{14} . CH_2 . NH (C_2H_5)_2 Cl \\ CH_3 (CH_2)_{14} . CH_2 . NH (C_2H_5)_2 \end{array}\right]^+ . Cl-$$
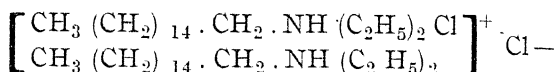
Typical of these substances are the Sapamines, Lissolamines, Fixanol, Velan, etc.; the basic dyestuffs also behave as typical cation-active substances.

A few auxiliary products are non-ionogenic, *i.e.* they do not ionise in solution to any extent and may, therefore, be considered as ionically neutral colloidal substances. Peregal O is of this type, as are auxiliary products of the type of lauryl pyridinium laurate.

The properties shown by solutions of the anion and cation-active substances differ considerably. Cation-active substances are absorbed by textile fibres which, in contact with aqueous solutions, usually possess a weak negative charge; these substances are, therefore, extremely useful as softening agents. Anion-active substances are not so absorbed, and are therefore not as good softening agents. On the other hand, in a neutral or slightly acid solution anion-active substances are much better scouring or washing agents than are the cation-active substances, since in such solutions the particles of dirt acquire a negative charge and so are repelled by the fibre, whereas in cation-active solutions they acquire a positive charge and are, therefore, attracted by the negatively charged fibres.

The behaviour of these two types of substances on both basic and direct cotton dyestuffs is also different. Thus, with the basic dyestuffs the anion-active substances tend to cause aggregation of the positively charged dyestuff so that if added to a basic dyebath they tend to cause aggregation giving a bronzy scum on the surface and encourage more rapid exhaustion. Cation-active substances, on the other hand, reduce any tendency to bronziness and exert a restraining action with these dyestuffs. Most cation-active substances when added to dyebaths. containing direct cotton dyestuffs tend to precipitate the dyestuff and so are unsuitable as dyebath additions for softening or other purposes. In practice, therefore, an after-treatment with such substances is essential. Anion-active substances do not cause any precipitation of direct cotton dyestuffs and may therefore be added to such dyebaths. Other distinctive properties of these two types of bodies are also dealt with later in this section.

Detergents and Lime-Soap Dispersing Agents.—The product most widely used in the treatment of textiles is soap, which when used in soft water is an excellent scouring, dispersing and emulsifying agent. Its principal defect, however, is its chemical instability. With hard water insoluble calcium and magnesium soaps are precipitated which not only waste the soap but become attached to the goods and result in stickiness, uneven dyeing, and in the case of rayons, partial " blinding " of the material. Although hard water may be softened by well-known water softening processes, no method is known whereby soap can be used under such acid conditions as obtain in certain dyebaths, as the acid " cracks " the soap, liberating free fatty acids having the same objectionable properties as the lime soaps. It is not surprising, therefore, that attempts should be made to make products having the desirable properties of the soaps without their defects.

The action of sulphuric acid on castor oil has been used for many years to prepare soluble, sulphonated or Turkey Red Oils. Turkey Red Oil, which is the sulphuric acid ester of ricinoleic acid, $C_{17}H_{32}SO_4H.COOH$, is more stable to hard water than soap, but its scouring, wetting and emulsifying properties are insignificant. It finds some application for the softening of cotton goods and also as a dyeing assistant in neutral or slightly

alkaline dyebaths. As it is only a partially sulphonated product it often causes trouble when used in hard water owing to the formation of insoluble sticky calcium salts, and when used in acid dyebaths is readily decomposed. Monopol soap is a more highly sulphonated product, but this product again has to a slightly less extent, all the undesirable properties of Turkey Red Oil. More recently highly sulphonated products such as Prestabit Oil V and Calsolene Oil HS have been placed on the market which, unlike Turkey Red Oil, are stable to hard water and are not precipitated by dilute solutions of mineral acids, but which again have no detergent properties. These products are finding an increasing application in the pigment padding process of vat dyeing (see p. 208). The percentage of the theoretically complete sulphonation reaction for the above products is given as :

Turkey Red Oil	..	..	..	.. 22 per cent.	
Monopol soaps ..	..	..	.	.. 39	,,
Avirol KM extra	..	..	..	.. 51	,,
Prestabit Oil V	..	..	..	.. 93	,,

Many auxiliary products consist of the highly sulphonated oils together with a solvent. Astol A, the solvent being trichlorethylene, is a typical example.

Another type of sulphonated product consists of the propyl, isopropyl, and isobutyl derivatives of naphthalene sulphonic acids and of sulphonates of tetrehydronaphthalene and octohydroanthracene. Nekal A, Nekal BX, Perminal W, Oranit, etc., are typical representatives of this group. These products, like the highly sulphonated oils, have good stability to hard water and to acid dyebaths, but lack detergent properties. Their main use appears to be as wetting agents. Many other auxiliaries consist of these products with a solvent, *e.g.* methyl cyclohexonal (Neomerpin), terpenes (Laventine BL), trichlorethylene (Eucarnit), etc.

The problem of the preparation of auxiliary products having detergent properties combined with resistance to hard water and acids has resulted in the development of a series of compounds which are probably the most important of all the recent textile auxiliary products. These newer detergents can be divided into the following three main types :

(1) Sulphated fatty alcohols, which are esters of the general type $R.O.SO_3Na$ represented by the Gardinols, Lissapol A, Sulphonated Lorol, etc.

(2) Fatty acid esters of the type $R.COO.C_2H_4SO_3Na$, *e.g.* Igepon A, which is the oleic ester of hydroxyethyl sodium sulphonate, $C_{17}H_{33}.CO.O.C_2H_4SO_3Na$. This is prepared by condensing oleic acid chloride with hydroxyethyl sulphonic acid. The product is then converted into the sodium salt and emulsified, using sodium phosphate to stabilize the emulsion.

(3) Fatty acid amides of the type $R.CO.NH.C_2H_4SO_3Na$, *e.g.* Igepon T, which is the oleic amide of hydroxyethyl sodium sulphonate, $C_{17}H_{33}.CO.NH.C_2H_4SO_3Na$, and is prepared by condensing oleic acid chloride with 2-chloroethylamine, and subsequently treating with sodium sulphite.

A series of products, the Igepals, have also been introduced which are stated to have been prepared synthetically and not from natural fats. In properties they are closely similar to the Igepons, but in certain respects, *i.e.* as wetting-out agents, are inferior to the latter.

Although these products can be chemically classified into three groups their properties and uses are, in general, very similar, although they vary somewhat in effectiveness. Thus, according to Briscoe (*J.S.D.C.*, 1933, p. 71), Sulphonated Lorol (sodium salt of sulphonated lauryl alcohol) has maximum wetting, penetrating and dispersing properties, whilst Sulphonated Ocenol (sodium salt of sulphonated oleyl alcohol) has maximum scouring and detergent properties. Again, Igepon A is unstable in hot alkaline liquors, whereas Igepon T is stable to alkalies. It is impossible in the space available to deal with all the claims which have been made for these products, and only one or two of their uses are discussed.

(*a*) *Wool Scouring.*—These products are finding an increasing use in wool scouring, and in back-washing liquors, whilst their stability to dilute acids has made possible the scouring and dyeing of single worsted yarns in cheese form.

(*b*) *Kier Boiling.*—The use of Igepon T, Lissapol LS and A in kier boiling is dealt with under this heading on p. 347.

(*c*) *Wetting-out of Cotton Yarns.*—As stated on p. 50, Igepon T has been found to be the best substance for the wetting-out of cotton condensor yarns.

(*d*) *Uses in Dyeing.*—In rayon yarn dyeing the authors have found that even when using " Permutit " softened water, an addition of Igepon T or Lissapol LS to direct cotton dyebaths containing soap and to soaping baths for the after-treatment of azoic and vat dyeings results in clearer dyebaths and so gives brighter yarns. Such an addition also acts as an insurance against trouble which may arise due to the capacity of the water softening plant being accidentally exceeded, or to · impurities which may get into the dyebath from the steam supply or from the rayon.

For further information on the uses of these auxiliary products the makers' literature should be consulted. (See also Briscoe, *J.S.D.C.*, 1933, p. 71 ; Kertess, *J.S.D.C.*, 1933, p. 69 ; 1936, p. 42 ; Dunbar, *J.S.D.C.*, 1934, p. 309 ; Hanney, *J.S.D.C.*, 1934, p. 273).

A lime-soap dispersing agent which differs from those previously described is Calgon, the main constituent of which is sodium hexametaphosphate $(NaPO_3)_6$. There is some evidence that its formula should be written $Na_2(Na_4P_6O_{18})$, indicating that all the metaphosphate radicles and four sodium atoms are in a complex. On adding a calcium salt to a solution of this substance the following reaction occurs :

$$2CaCl_2 + Na_2(Na_4P_6O_{18}) = 4NaCl + Na_2(Ca_2P_6O_{18})$$
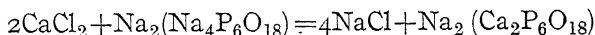
so that as the calcium is in the complex it does not show the ordinary reactions of a calcium salt. A similar reaction occurs with other calcium salts, including calcium soaps.

Calgon is supplied in colourless glass-like plates packed in 25 lb. bags ; for solution the bags are suspended in wooden or earthenware containers (metal vessels should be avoided) containing water at not above 35° C. sufficient to give a solution of convenient strength, *e.g.* a 25 per cent. solution.

This substance may be used in all cases where there is a liability to lime soap formation or for the removal of lime-soap

already present on textiles, for example, it may be added in loose wool scouring to the last soap bowl. Like Igepon T it acts as an insurance when using softened water against cases where the capacity of the softening plant is accidentally exceeded before regeneration. Calgon is also a useful addition to vat dyebaths to prevent dyestuff " riding " on the foam, and so reduces the possibility of " specky " dyeings. When added to soap liquors used for soaping sulphur, vat and azoic dyeings, a cleaner dyeing is obtained.

In any form of package-dyeing machine where the dyeliquor is circulated through the goods, an addition of Calgon disperses any metallic soap impurities present which would otherwise be filtered out of the dye-liquor and so give dirty dyeings ; it thus tends to eliminate one of the major difficulties experienced in this type of dyeing.

With iron and copper salts Calgon forms complex ions similar to those with calcium and magnesium salts. Use has been made of this property to prevent the dulling of shades of chrome dyestuffs due to (a) the presence of iron in the water used in dyeing (Bird and Molloy, *J.S.D.C.*, 1939, p. 560), and (b) the presence of iron as rust or when used in the construction of dyeing machines (*J.S.D.C.*, 1941, p. 224). These authors also find that acid sodium pyrophosphate, tetrasodium pyrophosphate, sodium tripolyphosphate and Trilon B are also successful to varying degrees for this purpose. Trilon A has also some protective action, but is much less effective than Trilon B. Kalle & Co. (E.P. 521,468) have suggested the use of Trilon A to protect amylases (*e.g.* pancreas) from the destructive action of traces of heavy metal salts frequently present in town water supplies. According to Bird, *J.S.D.C.*, 1940, p. 473) Trilon A is the sodium salt of a : a' : a''—trimethylamine tricarboxylic acid, and Trilon B the sodium salt of ethylene—bis—iminodiacetic acid.

Kier-Boiling Assistants.—Numerous substances of very diverse character have been suggested as additions to kier-boiling liquors, including emulsified tetrahydronaphthalene (Perpentol), pine oils (Perminal KB), trichlorethylene, etc. These products are alleged to offer advantages, such as improved handle, reduction in the time of boiling, etc., over boils made without such additions, but, although the technical literature on this

subject is very large, the claims made are seldom supported by comparative experimental data which allow a true assessment of their practical value. Expensive large-scale trials are therefore necessary before such products can be adopted, an expense which few firms are willing to bear in order to try out a recommendation by an interested party, particularly if their kier boiling is working satisfactorily. Again, it should also be remembered that with the present low prices ruling for kiering and bleaching the cost of many of the suggested kier-boiling assistants make their use uneconomical.

Practical tests of many of these products have shown that when using water softened by the Permutit process none of the products examined offered any advantage over the kiering liquor described on p. 50.

Where hard water only is available it is possible that the use of selected auxiliary products may prove advantageous. Thus it is claimed by the makers and supported by the following figures that the addition of Igepon T. offers many advantages.

The yarn used was an Egyptian yarn which was boiled for 4 hours at 20 lb. pressure using water of 15° hardness.

Boiling liquor	Clearing effect (whitening)	Reduction in weight	Ash residue, per cent.	Wetting out (time)	Permanganate No.
3 per cent. NaOH..	—	7·7	1·18	100 secs.	10
3 per cent. NaOH + 1 per cent. Igepon T	Best	7·9	1·10	6 secs.	6
Untreated	—	—	3·38	over 5 mins.	48

The low permanganate number is synonymous with a high degree of purity of the cellulose.

Scholefield and Ward (*J.S.D.C.*, 1935, p. 172) find that the addition of 0·2 per cent. Lissapol A paste (on the volume of liquor) to a caustic kier-boiling liquor exerts a favourable influence, particularly on the whiteness of the cloth and on the removal of fats, waxes, etc. Good whites were also obtained using as low as 0·05 per cent. solutions.

Wetting Agents for use in Mercerizing Liquors.—The addition of certain wetting agents to mercerizing liquors makes

it possible to mercerize grey yarns or cloths without the necessity of previously boiling out the material. By rendering unnecessary the lye-boiling of grey cotton a material with a softer handle is obtained owing to the higher wax content of the mercerized cotton, and dilution of the caustic soda solution by water from wet material is avoided. There is also an economic advantage in the elimination of a process, whilst, although these wetting agents have no influence on the mercerizing action of the caustic soda, they hasten contact between the caustic liquor and the fibre, and so reduce the possibility of uneven mercerization which may cause trouble in subsequent dyeing.

Most ordinary wetting agents are unsuitable for this purpose, since they are either unstable or insoluble in caustic soda solutions of mercerizing strength. A large number of substances have been examined, but it is now generally agreed that phenolic derivatives are the most suitable, so that these substances alone, or with the addition of a wetting agent, such as cyclohexanol, form the basis of most commercial products. Thus, Mercerol, is stated to contain cresol, cyclohexanol, xylene and a glycol derivative, whilst Perminal M.E.R.C. contains cresol, pine oil, and olein oil. Shirlacrol consists of the phenolic mixture from tar fractions, b.p. 205°–290° C. (see also Morgan, Pratt, and Pettet, *J.S.D.C.*, 1933, p. 125; E.P. 390,824). The quantity used in practice naturally varies somewhat with individual products, but in general not more than 2 per cent. of the volume of liquor is used to produce the maximum effect whilst in some cases 0·5–1·0 per cent. is effective. Some wetting agents are disproportionately absorbed during mercerizing so that the returned liquor is weaker in respect of wetting agent ; periodic checking of the quantity of wetting agent present is therefore necessary.

Vat Restraining and Levelling Agents.—The production of level, well penetrated dyeings of the vat dyestuffs is one of the major difficulties of the dyer, and has led to the introduction of numerous auxiliary products which are reputed to minimize this difficulty. As this problem is not due to the imperfect wetting out of the material the use of many of these products, whose main virtues are good wetting out properties, is useless. The difficulty of producing satisfactory vat dyeings is undoubtedly due to the great affinity of the leuco vat dyestuffs for the fibre,

resulting in the more accessible parts of the material absorbing most of the dyestuff from the dyebath so that only a weaker dye-liquor is available for the dyeing of the more sheltered parts. Hard twisted cotton yarns, tightly woven cloths, and viscose rayon skeins are typical cases which present great difficulties in obtaining satisfactory dyeings due to this cause. By making additions to the dye bath two methods of overcoming this difficulty are theoretically possible :

(1) To increase the levelling properties of the vat dyestuffs so as to allow of more rapid transference of dyestuff from the heavily dyed to the lighter dyed parts than normally occurs in the dyebath. Up to the present time the only class of substances which have been found capable of appreciably increasing the levelling properties of the vat dyestuffs are solvents. Although solvents have been suggested for this purpose the amounts which have been recommended are usually totally inadequate. Thus, of the solvents pyridine is undoubtedly one of the most effective, but 5–10 per cent. solutions are required to produce marked effects whilst with methylated spirit 20–25 per cent. solutions are required (see E.P. 467,662 ; E.P. 482,324). Such quantities are impracticable on the grounds of expense, so that at present this method offers no practical solution to the problem, unless recovery plant is installed.

(2) To reduce the affinity of the vat dyestuff for the fibre and so control exhaustion of the dyebath by the more accessible parts of the material. Most of the useful auxiliary products marketed as aids to penetration and level dyeing of the vat dyestuffs belong to this class, *e.g.* Peregal O and OK, Albatex PO, Repellat, certain cellulose waste liquors like Protectol II, etc. The chemical constitution of most of these products has not been given, but Peregal O is stated to be a non-ionic condensation product of octadecyl alcohol and ethylene oxide (probably E.P. 380,431) whilst Repellat (Kertess, *J.S.D.C.*, 1936, p. 43) is stated to be a substance of the type of dodecylpyridinium laurate. According to Forster (*J.S.D.C.*, 1940, p. 501) Albatex PO is a product of the type

$$\left[\begin{array}{c} CH_3(CH_2)_n O.OC- \\ HOOC- \end{array} \diagup\hspace{-0.3em}\bigcirc\hspace{-0.3em}\diagdown SO_3 \right]^{-} Na^+$$
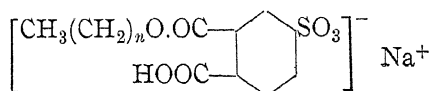
The mode of action of these substances is not very clear, but Peregal O is stated to form an unstable addition compound with the leuco vat dyestuff. In the case of direct cotton dyestuffs, measurements on the highly dispersed Chicago Blue 6B showed that the dissolved dyestuff molecules were changed to larger aggregates, the Peregal O serving to give centres for such aggregations. Whatever the mechanism it is obviously not the same as salting-out, although the explanation sounds like it. As a matter of fact, Peregal O, like many other of these substances, counteracts salting-out (see also Valkó, *J.S.D.C.*, 1939, p. 173).

When using these products the vat dyestuffs are vatted in the usual manner, the dyebath prepared, and the requisite amount of the well-diluted auxiliary product added immediately before use. It must be remembered that the use of these products usually requires more vat dyestuff to obtain the same depth of shade than in their absence. One of the main practical difficulties is that all vat dyestuffs are not equally restrained ; one dyestuff may be considerably restrained, whilst another may not be restrained at all. This difficulty has been accepted by most of the makers who issue lists showing the extent to which the various vat dyestuffs are restrained. When comparing the relative merits of vat restraining agents the strike tests described on p. 210 will be found of value.

Stripping Agents.—In order to correct faulty dyeings, it is sometimes necessary to remove most of the dyestuff from dyed materials ; this process is termed "stripping." Methods of stripping based on the use of reducing or oxidizing agents alone are effective with many dyestuffs, but are ineffective for stripping most vat and certain of the fastest azoic dyestuffs. To facilitate the stripping of such dyestuffs the addition to reducing baths of substances which act as stripping promoters has been suggested. Thus, a process for stripping vat dyeings which consists of treating the dyeings in a hot reducing bath containing a protective colloid and magnesium sulphate has been described by the I.G. (E.P. 409,336). A stripping promoter, Decamine A, now renamed Lissolamine A has also been described by Lawrie (*J.S.D.C.*, 1933, p. 309) and Dunbar (*ibid.*, 1934, p. 314) for stripping azoic dyeings. Lissolamine V is a similar product introduced for the stripping of vat dyeings. These products are cation-active long

chain quaternary ammonium salts. When using Lissolamine A (Rowe and Owen, *J.S.D.C.*, 1936, p. 305) azoic dyeings are treated with 3 per cent. caustic soda, 4 per cent. sodium hydrosulphite, and 2 per cent. Lissolamine V on the weight of material for $\frac{1}{2}$ hour at 90°–95° C. The resultant yellow shade of the material is removed by a mild bleach with $\frac{1}{4}$° Tw. sodium hypochlorite. With some azoic dyeings it is preferable to treat the material with the caustic soda and Lissolamine A at the boil for about ten minutes and then to add gradually the sodium hydrosulphite, the temperature being maintained for a further twenty minutes.

The stripping promoting action of the Lissolamine V varies considerably with different vat dyestuffs, but the shade is usually stripped sufficiently to allow of subsequent re-dyeing.

The material is treated for 30–45 minutes at 85°–90° C. in a bath containing 3–5 per cent. Lissolamine V and 4–6 per cent. caustic soda, 6 per cent. sodium hydrosulphite powder. After treatment it is rinsed in cold water and chemicked as described for azoic dyeings.

Before re-dyeing material stripped with these products it is advisable to soap at the boil to ensure the complete removal of residual traces of Lissolamine A or V.

An interesting method of stripping vat dyeings has been suggested by Du Ponts (A.P. 2,206,535) which uses alkali and formamidine sulphinic acid, prepared by the action of hydrogen peroxide on thiourea, at a temperature near the boiling point.

Products for Increasing the Fastness of Direct Cotton Dyestuffs to Water, Acid Cross-dyeing, etc.—In recent years a number of auxiliary products have been marketed for after-treating direct cotton dyeings so as to give them an increased fastness to water, acid cross-dyeing, perspiration, and damp ironing. Typical examples of such products are Fixanol, Solidogen B, Sandofix, Lyofix DE, and the Sapamines. According to the literature Fixanol is a quaternary ammonium compound, probably cetyl or octadecyl pyridinium bromide (E.P. 398,175), Solidogen B and BCE and Sandofix are probably covered by E.P. 435,388 and 464,921 respectively (see Mehla and Trivedi, *J.S.D.C.*, 1940, p. 344). Sapamine CH is the hydrochloride, Sapamine A the acetate, Sapamine CH the methosulphate, and

Sapamine BCH the benzyl hydrochloride of oleyl diethylamino-ethylamide, whilst Sapamine KW is stated to be mono-oleyl asymmetric methyl diethylene-diamine metho sulphate. Lyofix DE is also a Sapamine type of compound (Forster, *J.S.D.C.*, 1940, p. 500).

These substances are cation-active having a strong affinity for vegetable fibres and, in general, form precipitates with direct cotton dyestuffs, which is the reason for the increased fastness to water, acid cross-dyeing, etc., obtained by such an after-treatment. The dyestuff-cation-active substance complex is destroyed by anion-active substances, such as soap or Igepon, so that the after-treatment does not increase the fastness to washing of dyeings so treated. All direct cotton dyestuffs are not equally increased in fastness by this treatment, whilst the shade of many is altered, so that the manufacturers have found it necessary to give lists of dyestuffs which are particularly suitable. It should also be remembered that in many cases the light fastness of the dyestuff is adversely affected. The method of after-treatment is very simple, and consists in treating the rinsed dyeing in the case of vegetable fibres with $\frac{1}{2}$–1 per cent. of the cation-active substance for 15–20 minutes at 20°–40° C. and in the case of wool-cotton unions with 1–2 per cent. cation-active substance for 20–30 minutes cold, and finally rinsing. Union materials may then be cross-dyed with little or no bleeding of dyestuff from the cotton to the wool, whilst in the case of, for example, cotton and rayon linings required to be fast to perspiration the material is simply dried. Prints and discharge prints when after-treated with cation-active substances show a greatly improved fastness to water, so that when they are rinsed in water there is no staining of white portions of the fabric.

Softening Agents.—Dyed textiles frequently require to be softened in order to improve their handle and draping qualities, or in the case of yarns, to facilitate knitting, and for this purpose soap, sulphonated oils, oil emulsions, etc., have been used for many years. During the past few years a new class of softening agents has been developed, viz : the cation-active softening agents, which in most cases produce an effect superior to that given by the older softening agents. Some idea of the interest shown in this type of substance as finishing agents is indicated by the fact

that during the first six months of 1941 over 65 per cent. of the total rayon produced (243,000,000 lb.) in the U.S.A. was treated with cation-active substances (Ackley, Amer. Dyes. Rep., 1941, p. 462).

As a softening agent, Sapamine KW used as an after-treatment has been particularly successful, a very small quantity, 0·1–0·5 gram per litre, only being required to give a very pronounced improvement in handle. Since anion-active substances tend to precipitate Sapamine KW it is obvious that this substance is most efficient as a softening agent if the material is free from soap, etc. (see also Forster, *J.S.D.C.*, 1940, p. 497). With some dyestuffs the treatment produces a shade change, the new shade being generally fuller and brighter than the original one. The light fastness of the dyeing may also be adversely affected, but this may be overcome by the simultaneous application of copper salts (" The Dyer," 1941, Vol. 85, p. 331).

Other products which are recommended as softening agents are the Soromines, Cirrasol, Ceramines, etc.

Water-Repellent Finishes.—The older methods of treating cloth to make it water-repellent consist of impregnating with metallic salts, for example, with basic aluminium acetate, followed by a treatment with a soap solution whereby the fibres become coated with the water-repellent aluminium compound of the fatty acid, or of impregnation with wax applied to the material either in a melted condition or dissolved in a solvent such as benzine. These processes have now been replaced to some extent by treatment of the material with wax emulsions or wax emulsions to which aluminium acetate has been added. Typical products of this type are the 30 per cent. wax emulsions Migasol PJ, Ramasit KW, and Waxol. Depending on the product, and on the conditions of application, 1–3 per cent. solutions of these emulsions are used, the impregnation being carried out at 20°–30° C. after which the material is squeezed or hydro-extracted and dried. If a slight sizing is required substances such as dextrine or gelatine, but not gum arabic, can be incorporated in the waterproofing solution.

In 1937 it was announced by the I.C.I. that water-repellent finishes can be applied to fabrics by treatment of the fabric with Velan PF, the active constituent of which appears to be a cation-

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active pyridinium compound, probably octadecyl-oxymethyl pyridinium chloride.

The method of application is to impregnate the material with a 1–4 per cent. Velan PF solution containing sodium acetate, squeeze or hydro-extract, dry, and then to heat for a short time at 100°–150° C. This heating should preferably be carried out in a hot air chamber, but drying cylinders may be used if the necessary conditions of time and temperature are observed. The period of heating required varies inversely with the temperature, *e.g.* at 100° C. the heating should be for 3–5 minutes, whereas at 120° C. 3 minutes and at 150° C. 1 minute heating is considered sufficient. After heating, the goods are given a light soaping for a few minutes in a liquor at 40° C., containing about 2 lb. soap and 1 lb. soda ash per 100 gallons. It should be noted that residual soap or other detergents left in the material reduces the apparent water-repellency, so that a thorough rinsing after soaping should be given.

The finishes produced by Velan give the goods an exceedingly soft handle, but their outstanding feature is that they are fast to washing, including treatment with boiling soap, and to dry cleaning, whilst the pores of the cloth are not blocked up. This process can be successfully combined with the anti-crease process to produce fabrics having the desirable properties conferred by both of these processes.

Emulsifying Agents.—A large number of auxiliary products have been introduced as emulsifying agents to faciliate the production of, and to increase the stability of oil emulsions, *e.g.* Amoa, Nekal AEM, Triethanolamine soaps, etc. In the textile industry the use of such oil emulsions appears to be mainly confined to their use as softening and, to a less extent, as sizing agents.

Miscellaneous Products.—Auxiliary products have also been marketed for many purposes other than those already described, including :—

(*a*) Wetting-out agents such as the Nekals, Perminal, Invadines, Igepons, Gardinols, etc.

(*b*) Mordants, such as Katanol, Resistone, Taninol, etc. (see p. 89).

(c) Antiseptics such as Shirlan (salicylic anilide), used for the prevention of mildew.

(d) Products for reserving animal fibres in union dyeing, such as Katanol WS, etc. (see p. 294).

(e) Dispersing agents, such as Diazopon A (see p. 178).

(f) Moth-proofing agents, such as Eulan, Mitin, etc.

(g) Permanent finishing agents, Bedafins, etc.

For further details of the auxiliary products the following references may be consulted.

Hetzer, " Textilhilfsmittel," Tabellen, 1938.

Chwala, " Textilhilfsmittel," 1939.

" Textile Auxiliaries and Assistants," Silk and Rayon, 1936, p. 690, which starts a serial list of products.

" Detergent, Emulsifying, Finishing and Wetting Agents," Goldthwait " American Dyestuffs Reporter."

" The Principles and Practice of Textile Printing," Knecht and Forthergill, 1936, gives a list of over 100 textile auxiliaries.

BIBLIOGRAPHY

THE student should realize that the necessarily abbreviated statements in text-books such as this are based on practical observations and on original investigations, so that for more complete information on certain aspects of dyeing it is often necessary to refer to other treatises and to original publications. The following list of treatises will be found useful for this purpose.

ASTBURY. Fundamentals of Fibre Structure.
BROWN. Modern Dyeing and Cleaning Practice.
BURTON and ROBERTSHAW. Sulphated Oils and Allied Products.
CARTER. The Bleaching, Dyeing and Finishing of Flax, Hemp and Jute Yarns and Fabrics.
CHWALA. Textilhilsmittel.
CLAYTON. Identification of Dyes on Textile Fibres and Detection of Metals in Fibrous materials, Dyes and Organic Pigments.
CURTIS. Artificial Organic Pigments.
EPPENDAHL. Betriebspraxis der Baumwollsträngfarberie.
ERFURT. Dyeing of Paper Pulp.
FARADAY SOCIETY DISCUSSION, 1932. Colloid Aspects of Textile Materials and Related Topics.
GREEN. Analysis of Dyestuffs.
HALL. Textile Bleaching, Dyeing, Printing and Finishing Machinery.
HEERMAN. Dyers' Materials.
HERZOG. Reactionstabelle der Kupenfärbstoffe und Indigosole.
HETZER. Textile-Hilfsmittel Tabellen.
HEUSER. Die Apparatfärberei.
HIGGINS. Bleaching.
HORSFALL and LAWRIE. Dyeing of Textile Fibres.
HOTTENROTH. Artificial Silk.
HÜBNER. Bleaching and Dyeing of Fibrous materials.
JORDON LLOYD and SHORE. Chemistry of the Proteins.
JUSTIN-MUELLER. Les Phénomènes de Teinture.
KIND. Das Bleichen der Pflanzenfasern.
KNECHT and FOTHERGILL. The Principles and Practice of Calico Printing.
KNECHT, RAWSON, and LOWENTHAL. A Manual of Dyeing.
LAMB. Leather Dressing.
LEY. Die Neuzeitliche Seidenfärberei.
LIPSCOMB. Cellulose Acetate ; its Manufacture and Application.
MARSH. Mercerising.
MARSH and WOOD. An Introduction to Cellulose Chemistry.
MATTHEWS. Application of Dyestuffs.
MATTHEWS. Bleaching and Related Processes.
MAUERSBERGER and SCHWARZ. Rayon and Staple Fibre Handbook.
MITCHELL and PRIDEAUX. Fibres used in Textile and Allied Industries.
MULLIN. Acetate Silk and its Dyes.
E. NOELTING and LEHNE. Aniline Black and its Application in Dyeing and Printing.
PATERSON. The Colour Printing of Carpet Yarns.

REINTHALER. (Translated F. M. Rowe.) Artificial Silk.
ROWE. The Development of the Chemistry of Commercial Synthetic Dyes (1856–1938).
SCHOFIELD AND SCHOFIELD. Finishing of Wool Goods.
SKINKLE. Textile Testing.
SOCIETY OF DYERS AND COLOURISTS. The Colour Index.
STEINBECK. Bleichen und Farben der Seide und Halbseide.
THORPE and LINSTEAD. The Synthetic Dyestuffs and Intermediate Products.
TROTMAN and TROTMAN. The Bleaching, Dyeing and Chemical Technology of Textile Fibres.
ULLMAN. Die Apparatfarberei.
VALKÓ. Kolloid-Chemische Grundlagen der Textilvereddlung.
WELTZIEN. Chemische and Physikalische Technologie der Kunsteiden.
WHEELER. Manufacture of Artificial Silk.
WHITTAKER. The Testing of Dyestuffs in the Laboratory.
WILLIAMS. Textiles on Test.
WOOD. Chemistry of Dyeing.
WOODHOUSE. Artificial Silk.
ZÄNKER. Die Farberie.

In addition to the above a very large amount of literature is distributed gratis by the dyestuff manufacturers. Whilst this is naturally confined to the individual manufacturers own dyestuffs the methods described will be found to be reliable and up to date.

More recent papers on dyeing should be sought in the various abstracts, the more important being

British Chemical Abstracts B ; Applied Chemistry (Before 1924, corresponding abstracts are to be found in the Journal of the Society of Chemical Industry).

British Cotton Industry Research Association Summary of Current Literature.

It may be pointed out that abstracts, however, well prepared, are only a rough guide to the contents of the original papers themselves, so that the latter should be consulted wherever possible. The more important journals in which dyeing investigations and current views on dyeing are published are the following :

The Dyer.
The Journal of the Society of Dyers and Colourists.
The Journal of the Society of Chemical Industry.
The Journal of the Textile Institute.
Melliand's Textilberichte (German and English editions).
American Dyestuff Reporter.
Textile World (U.S.A.).
Rayon and Melliand Textile Monthly.
The Silk Journal.
The Textile Recorder.
The Textile Manufacturer.

Die Kuntside.
Rusta.
The Textile Mercury and Argus.
Revue Generale des Matières Colorantes.
Deutsche Färber Kalender.
Deutsche Färber Zeitung.
The Textile Weekly.
Silk and Rayon.
The Textile Colorist (U.S.A.).
Leipziger Färber Zeitung.

In addition it should be remembered that membership of the various Research Associations dealing with textiles entitles one to their confidential publications.

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